

GRIDLEY

Hydroxylamine, its Quantitative
Determination and
Some Double Salts

Chemistry

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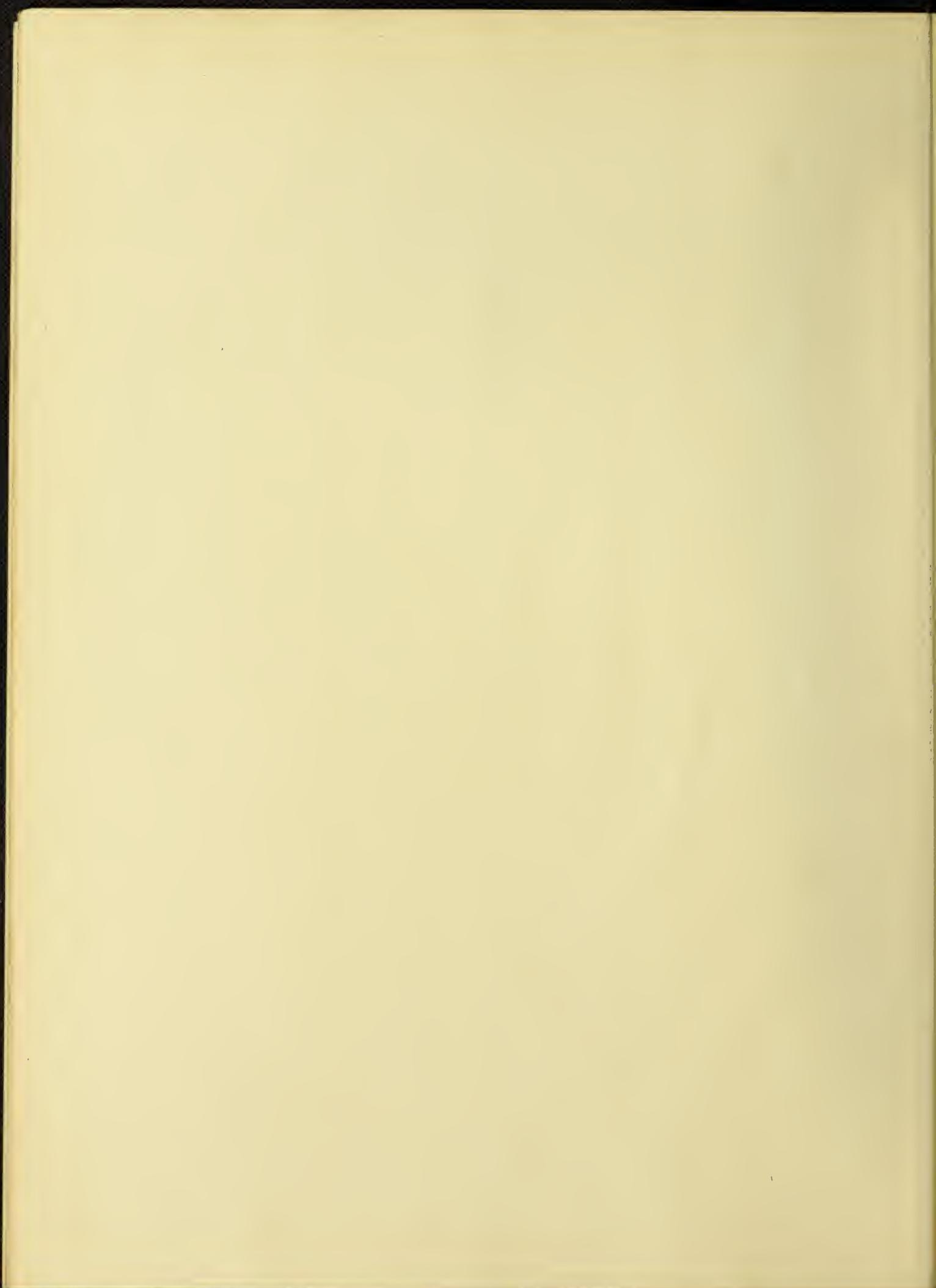
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HYDROXYLAMINE, ITS QUANTITATIVE DETERMI-
NATION AND SOME DOUBLE SALTS

BY

MABEL A. GRIDLEY

THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

IN THE

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Mabel A. Gridley

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DEGREE OF

Bachelor of Science

Helen Dohane.

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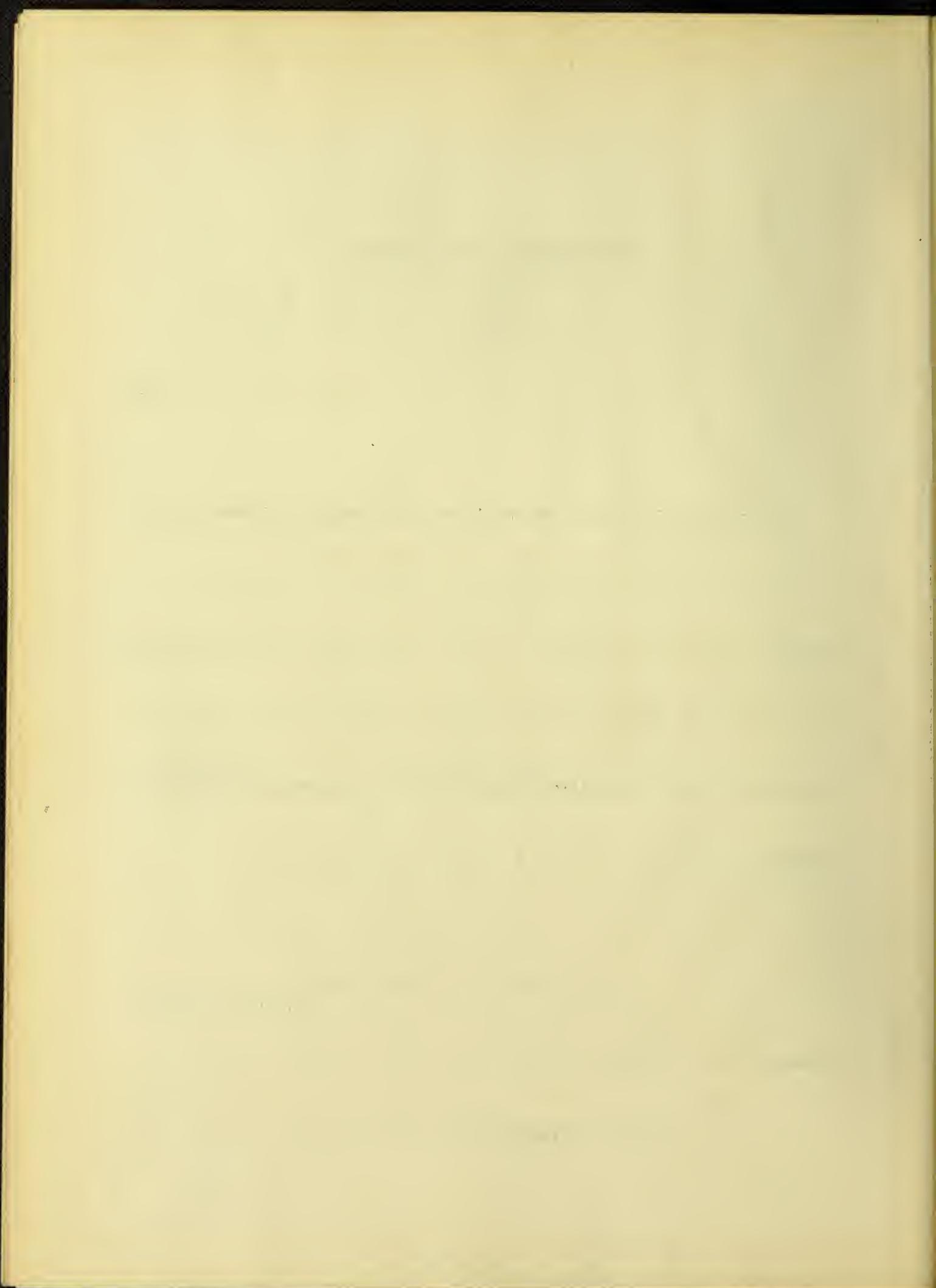
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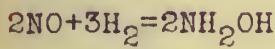
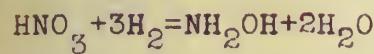
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Chemistry

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Hydroxylamine, NH_2OH is formed by the action of nascent hydrogen upon nitric acid, the oxides of nitrogen or the nitrates.



The nascent hydrogen is evolved from tin and hydrochloric acid and a stream of nitric oxide passed through the mixture. The hydroxylamine thus formed is purified by passing hydrogen sulphide through the solution. The tin is precipitated as the sulphide and removed by filtration. The filtered solution is then evaporated to dryness and the hydrochloride of hydroxylamine $\text{NH}_2\text{OH} \cdot \text{HCl}$ is dissolved out of the residue by means of absolute alcohol. The latter is distilled off and the residue is converted into the sulphate by treating with sulphuric acid.

Hydroxylamine is also prepared by boiling potassium hydroxylamine disulphonate with water.



The potassium sulphate is removed by crystallization. The hydroxylamine can be obtained in solution from the sulphate by the addition of barium hydroxide.

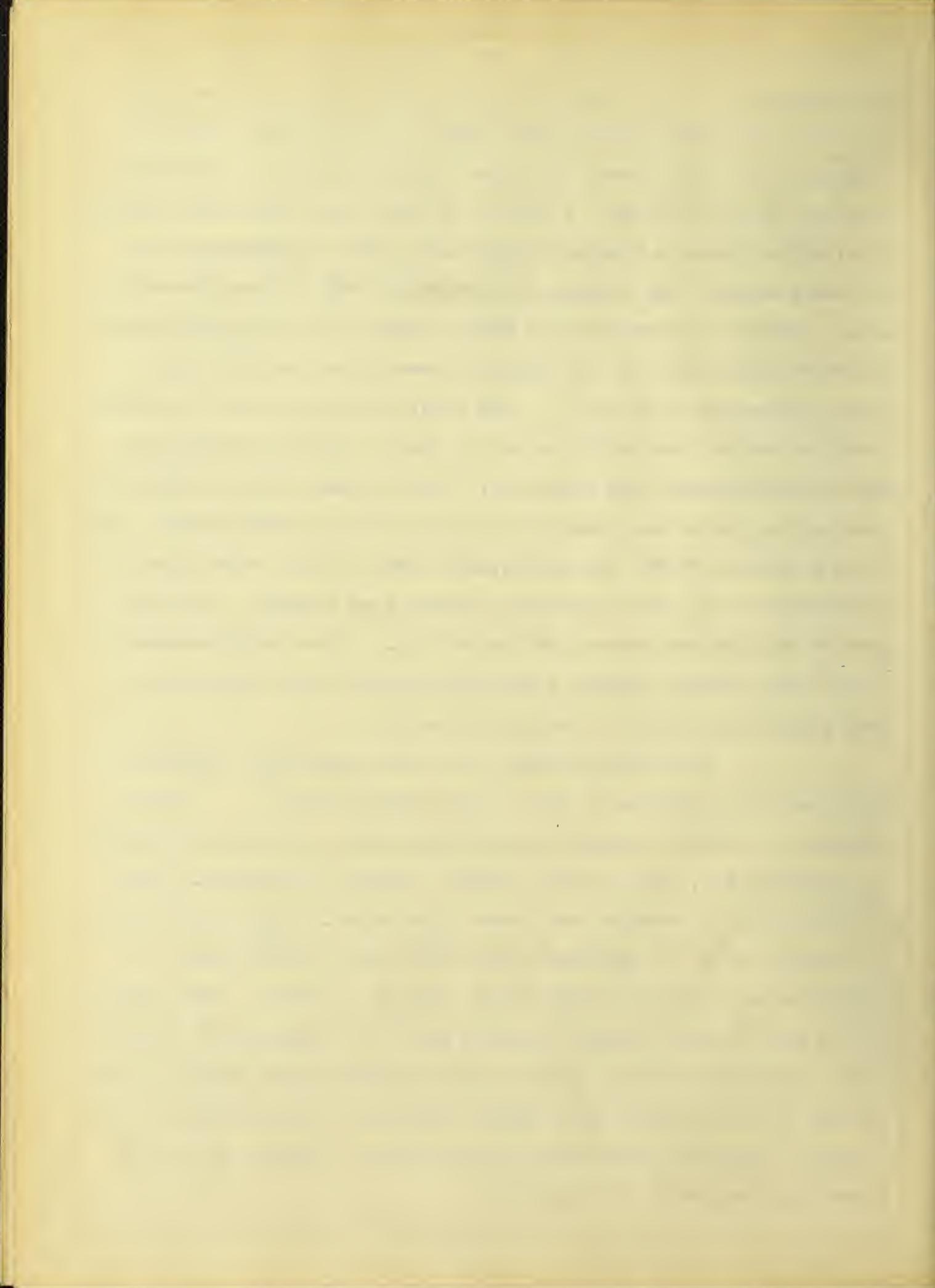
+C. A. Lobry de Bruyn prepared hydroxylamine in the following manner:-One hundred grams of hydroxylamine hydrochloride were dissolved in six hundred c.c. of absolute methyl alcohol at a gentle heat. The calculated quantity, to leave hydroxylamine hydrochloride in slight excess, of a concentrated solution of sodium methyl oxide was then added while the solution was still hot, the sodium chloride was filtered off and the filtrate was distilled at

+Ber. 27, 967-970

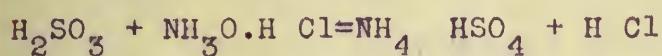


a pressure of from 160-200 m.m. The alcohol carried over little hydroxylamine at this reduced pressure. When most of the alcohol had distilled over, dry ether was added to the residue. This now separates into two layers, the upper containing 5.5% of hydroxylamine and the lower 53.5%. A portion of the lower layer was separately distilled under a pressure of 165 m.m. until a temperature of 86° was reached. The residue then contained 70% of free hydroxylamine. After an interval of six weeks, during which time some decomposition took place, all the solutions were mixed and distilled under a pressure of 60 m.m. The first portions of the distillate contained ammonia and methyl alcohol, then a fraction containing 32% of hydroxylamine was collected. The residue containing 80% of free hydroxylamine was fractionally separated into three parts. The first contained 27.2%, the second, about 60%, and the third portion solidified in the cooled receiver forming long needles. The last part of this passed over at 70° and 60 m.m. The solid substance after being pressed between filter paper gave a hard crystalline mass containing 99.4% of free hydroxylamine.

Free hydroxylamine is a very hygroscopic substance, which rapidly liquefies in the air and melts at 27.5°. Sodium chloride is readily dissolved by hydroxylamine, in these properties it resembles ice. Free sodium attacks the solid violently. Free hydroxylamine is odorless and denser than water. When heated rapidly on platinum foul, it explodes with a fine clear yellow flame. It dissolves very little in chloroform, benzine or ether. When exposed to the air the solid first liquefies and then disappears by evaporation. The hydroxylamine, melted forms a rather thick liquid, a sixty percent solution shaken with methyl iodide and methyl alcohol forms a white crystalline mass after several hours. Bromine and iodine attack hydroxylamine with violence.



+When a 10% solution of hydroxylamine hydrochloride or sulphate is saturated with sulphurous anhydride and evaporated, ammonium sulphate is formed-



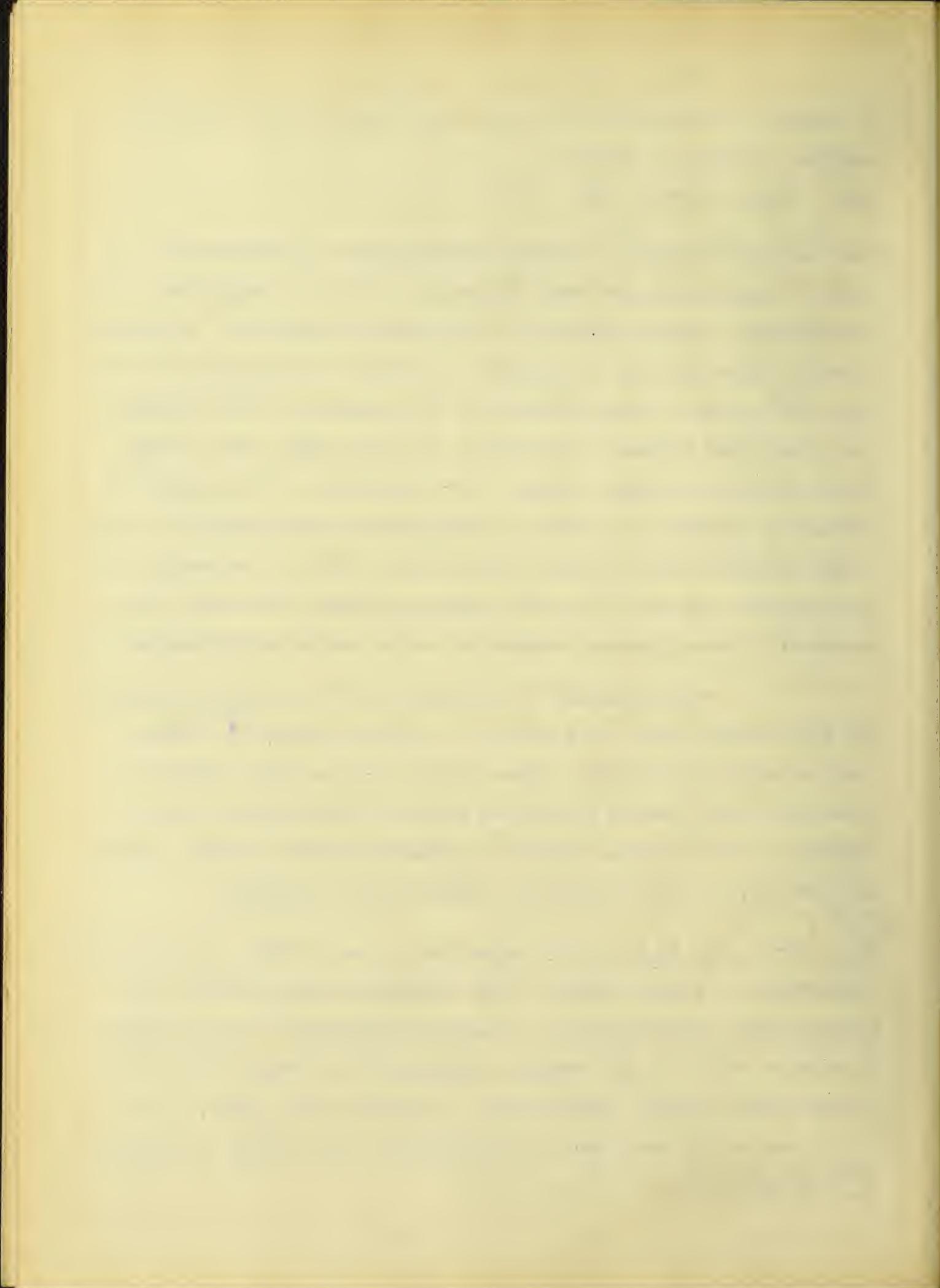
When the hydrochloride is warmed with phosphorus pentachloride , a reaction takes place and when the water solution is evaporated, the hydroxylamine has been converted into ammonium chloride. By hydrogen peroxide, hydroxylamine is oxidized directly to nitrogen and nitric acid, the oxidation being carried out in presence of sodium hydroxide. The chief product of oxidation is nitric acid, only a small amount of nitrogen being formed. The experiment of the action of sulphurous anhydride on aqueous hydroxylamine hydrochloride is criticized by Rasching and Bruhl, who point out that in the change the hydroxylamine does not act as an oxidizing agent, but simply condenses with the sulphurous anhydride, which undergoes hydrolysis.

+ Hydroxylamine is decomposed in the presence of hydrogen ferrocyanide with the formation of violet crystals of ferrocyanide and nitro prusside. When boiled with an equal weight of potassium ferro cyanide in aqueous solution hydroxylamine hydrochloride yields ammonium chloride, potassium nitro prusside, hydrogen cyanide, nitrogen and ferric ammonium ferro cyanide.

$\text{Fe}_2 \left[(\text{Fe C}_6 \text{N}_6) \text{NH}_4 \right]_2$, which separates out as a deep blue crystalline powder of purple lustre. This compound is also formed when hydroxylamine hydrochloride is boiled with potassium ferri-cyanide in aqueous solution, and remains unchanged when treated with water, dilute mineral acids, oxalic acid, or glacial acetic acid. The color remains the same when the crystalline violet salt is digested

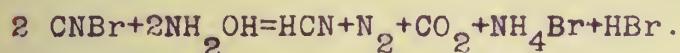
+Ber. 32, 241-45

+Ber 39, 2204-2208

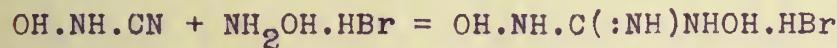
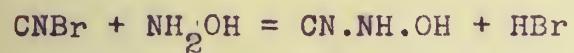


with 4% ammonium hydroxide solution. The quantitative experiment shows that one-half is converted into nitro prusside, and the other half into ferric-ammonium ferro-cyanide.

+The action of CNBr on hydroxylamine is almost explosive.

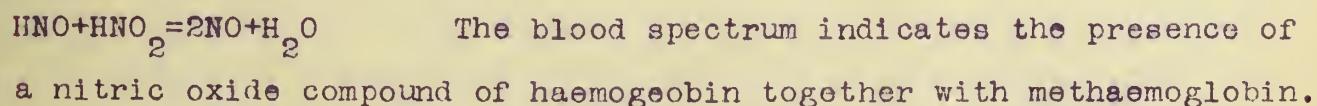
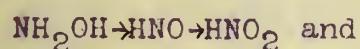
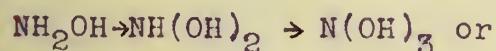


The reaction is modified by working at a temperature of -20° and with the compounds dissolved in a mixture of absolute methyl alcohol and ether. Then a 75% solution yields di-hydroxy-guanidine hydro-bromide $\text{OH} \cdot \text{NH} \cdot \text{C}(\text{NH})\text{NH} \cdot \text{OH} \cdot \text{HBr}$. The action probably takes place as follows:-



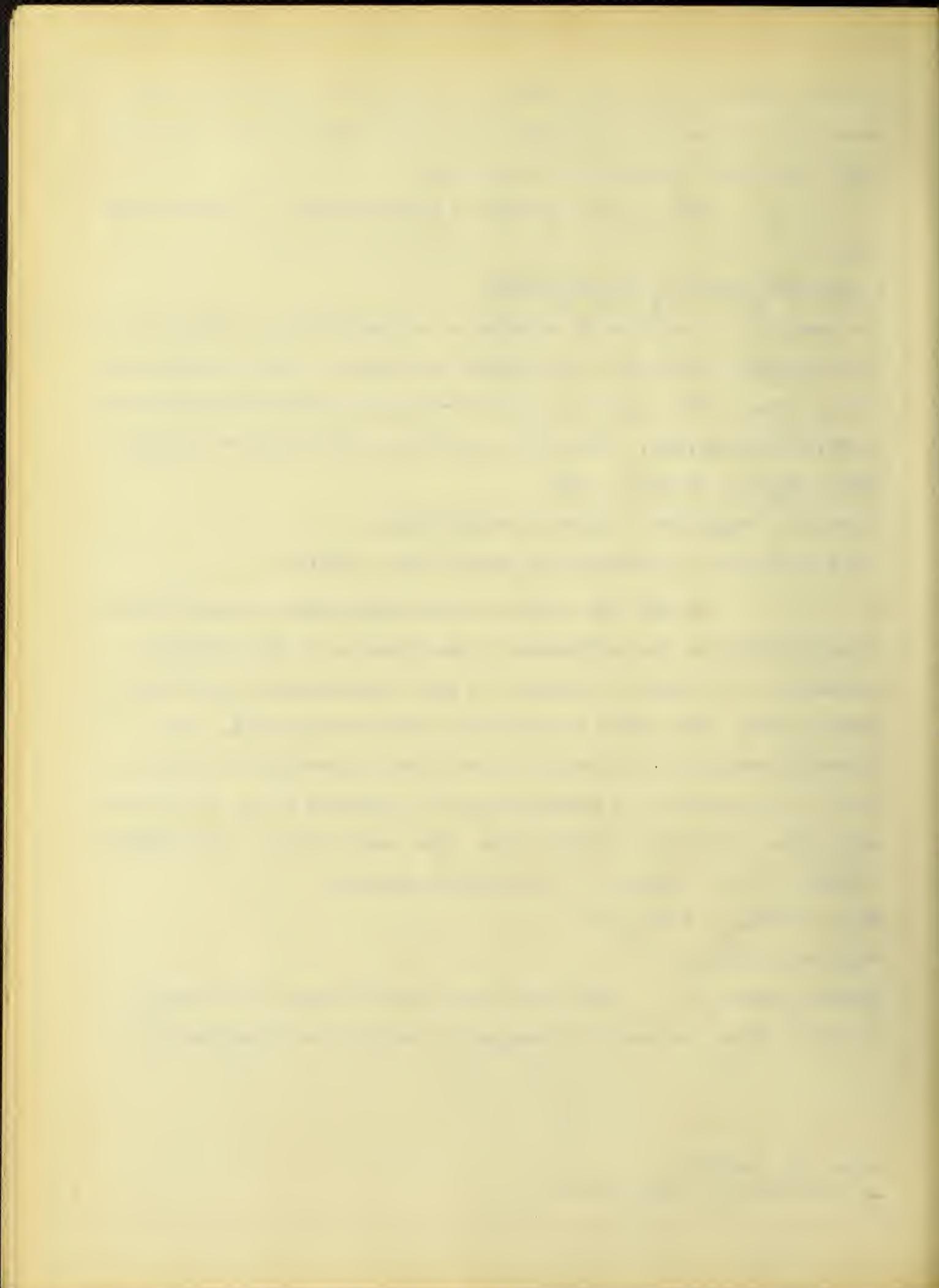
The crystals are colorless flat hygroscopic needles.

\pm Cinsa and Luzzatto made experiments on the toxicity of hydroxylamine, the influence of its presence on the oxidation products in the urine of animals to which hydroxylamine had been administered. The blood was examined spectroscopically. As a poison hydroxylamine is four or five times as powerful as nitrous acid. In the blood the hydroxylamine is oxidized first to nitrous acid, then reduced to nitric oxide. The most probable intermediate action is the formation of di-hydroxyl ammonia.



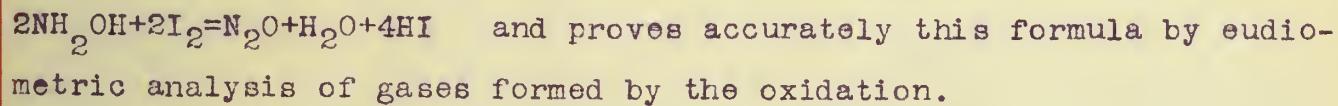
⁺Ber. 38, 1445-61

\pm J. of Chem. Soc. Ab. 94, 876



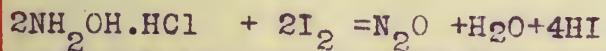
Quantitative Determinations

The method of Meyen^t in which the hydroxylamine was determined by titration with free iodine in presence of sodium phosphate and Magnesium oxide (MgO) was tried. The oxidation reaction is quantitative only when one is careful to neutralize the hydriodic acid formed. Potassium carbonate is not alkaline enough to completely neutralize the acid but either sodium phosphate or magnesium oxide work well. To the hydroxylamine solution, add sufficient amount of sodium phosphate and a slight excess of iodine solution and titrate back with sodium thiosulphate. If the amounts of hydroxylamine and used iodine are figured from atomic weights, one molecule of hydroxylamine salt requires two atoms of iodine. It follows that one molecule of hydroxylamine is oxidized by two atoms of iodine if the hydriodic acid formed is neutralized at once,

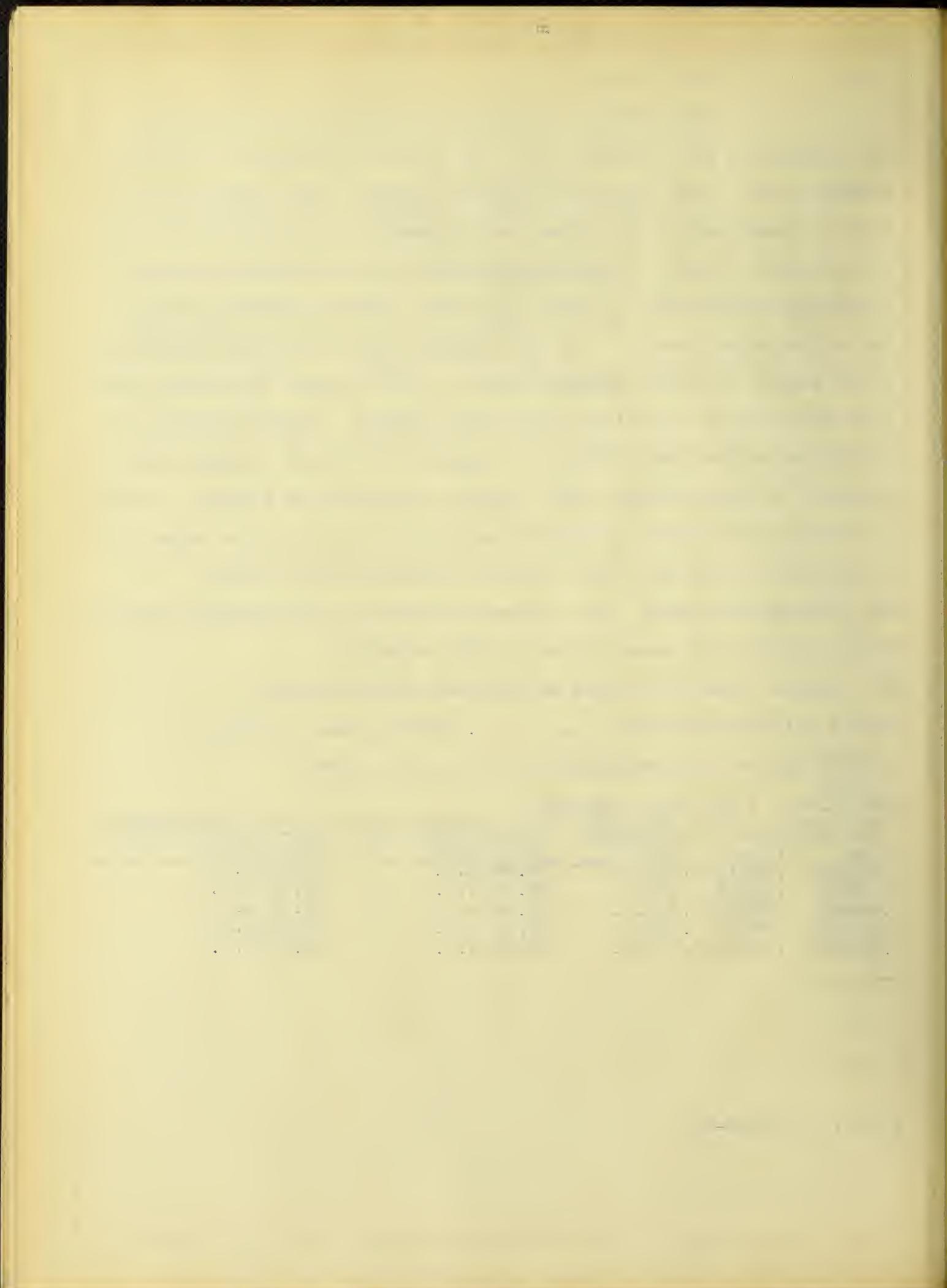


The results obtained by this method were unsatisfactory.

Iodine solution of which 1 c.c. = $\frac{1}{2}$.007676 grams of iodine = $\frac{1}{2}$.0009972 grams of hydroxylamine per c.c., was used.



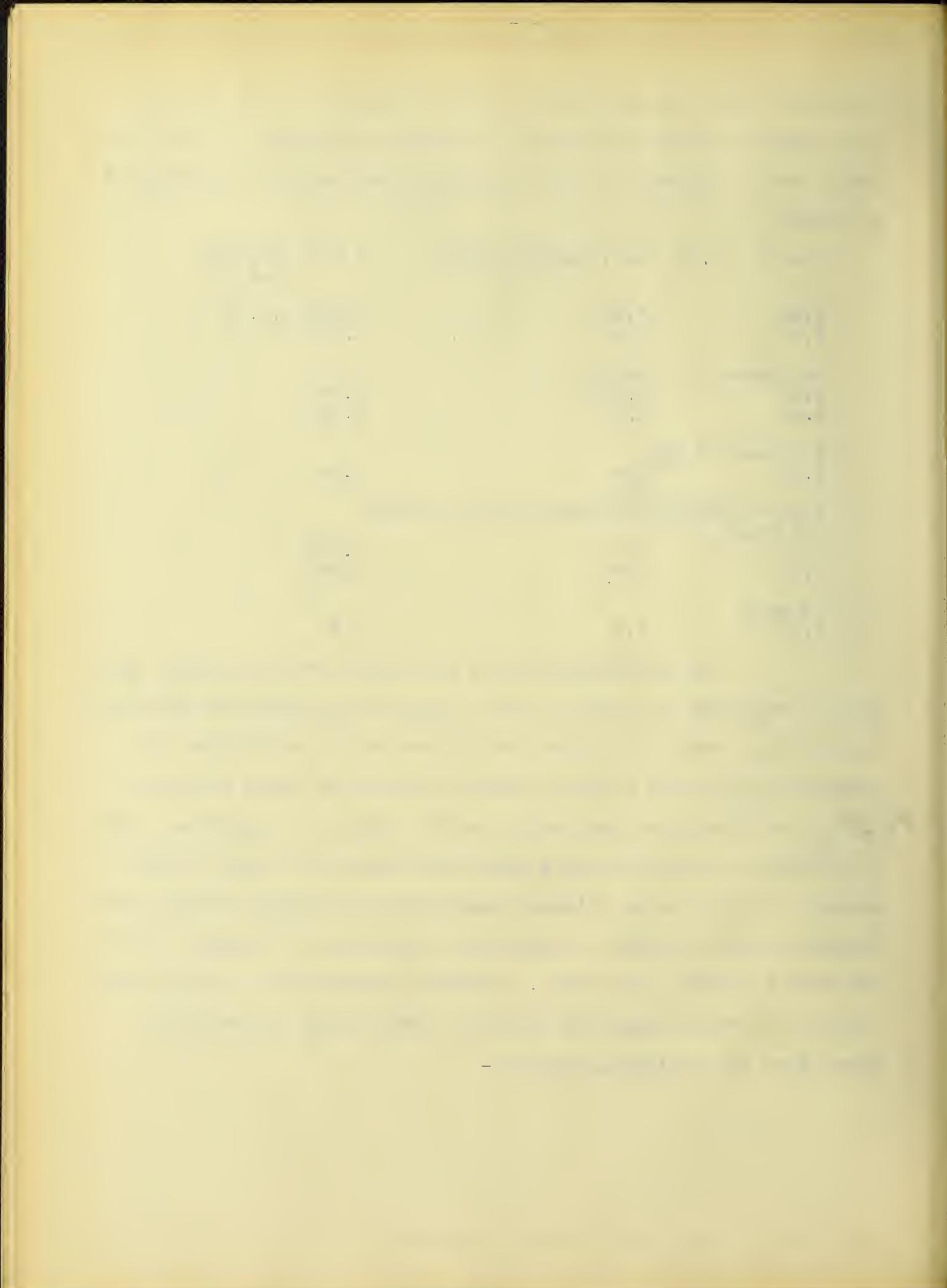
| Wt. NH ₂ OH.HCl taken | c.c. Na ₂ S ₂ O ₃ used | c.c. of Iodine solution taken | c.c. of Iodine solution used |
|----------------------------------|---|-------------------------------|------------------------------|
| 1.0496g. | .0341g | 3.4 c.c. | 16.25 c.c. |
| 2.0985g. | .1155g | 1.55 c.c. | 55.00 c.c. |
| 3.0398g. | .0473g | 2.3 c.c. | 22.55 c.c. |
| 4.0316g. | .0378g | .85 c.c. | 18.00 c.c. |
| 5.0622g. | .0703g | 2.9 c.c. | 33.85 c.c. |



In numbers one, two, and three sodium phosphate, and in four and five magnesium oxide was used as a neutralizing agent. A test was run to see if titration with thiosulphate was accurate in presence of alkali.

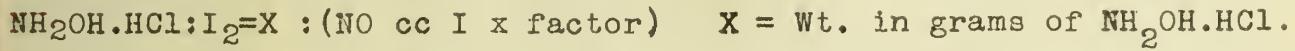
| c.c. of I used | c.c. $\text{Na}_2\text{S}_2\text{O}_3$ used | 1 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ $= \frac{1}{2}$ c.c. I. |
|--|---|---|
| 3.24 | 2.34 | 1.384 c.c. I |
| 3.1 | 2.25 | 1.380 " " " |
| In presence of Na_3PO_4 | | |
| 4.1 | 1.55 | 2.64 |
| 5.4 | 2.34 | 2.307 |
| In presence MgO | | |
| 6.5 | 3.2 | 2.03 |
| is added When H_2SO_4 to neutralize the excess of Na_3PO_4 | | |
| 3 | 1.85 | 1.621 |
| 2.2 | 1.70 | 1.293 |
| of MgO | | |
| 2.5 | 1.9 | 1.32 |

The determination was as follows:-To the weighed portion of $\text{NH}_2\text{OH} \cdot \text{HCl}$ an excess of the neutralizing agent was added and the solution made up to about one hundred cubic centimeters and immediately titrated with the iodine solution of known strength, it was found from the tests that the object is to get as small an excess of the neutralizing agent as possible and also a small excess of iodine to be titrated back with thiosulphate because when sulphuric acid is added to neutralize any excess of alkali, it will set free hydriodic acid again. Further determinations with iodine solution in which magnesium oxide was used as the neutralizing agent gave the following results:-



| No. of Expt. | Wt. NH ₂ OH.HCl taken | c.c. of Iodine taken | c.c. of Na ₂ S ₂ O ₃ used |
|--------------|----------------------------------|----------------------|--|
| 1 | .0122g | .01474g | 10.85 |
| 2 | .0770g | .0705 g | 36.7 |
| 3 | .0779g | .0768 g | 39.25 |
| 4 | .0863g | .0858 g | 42.41 |
| 5 | .0411g | .0395 g | 21.5 |
| | | | 19.03 |
| | | | 3.25 |

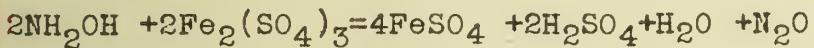
To calculate --



+The next method tried was the reduction of ferric sulphate with hydroxylamine and the estimation of the ferrous salt with known permanganate solution. +Ebler and Schott use this method and claim to get good results . About one-tenth of a gram of the hydroxylamine salt is dissolved in a little water and a known weight of ferric sulphate and a few c.c. of sulphuric acid are added. The solution is heated to 90° and kept at that temperature for five minutes. The hydroxylamine in hot acid solution is oxidized by means of ferric salts to nitrous oxide and water.



and an equivalent amount of ferrous salts are formed.



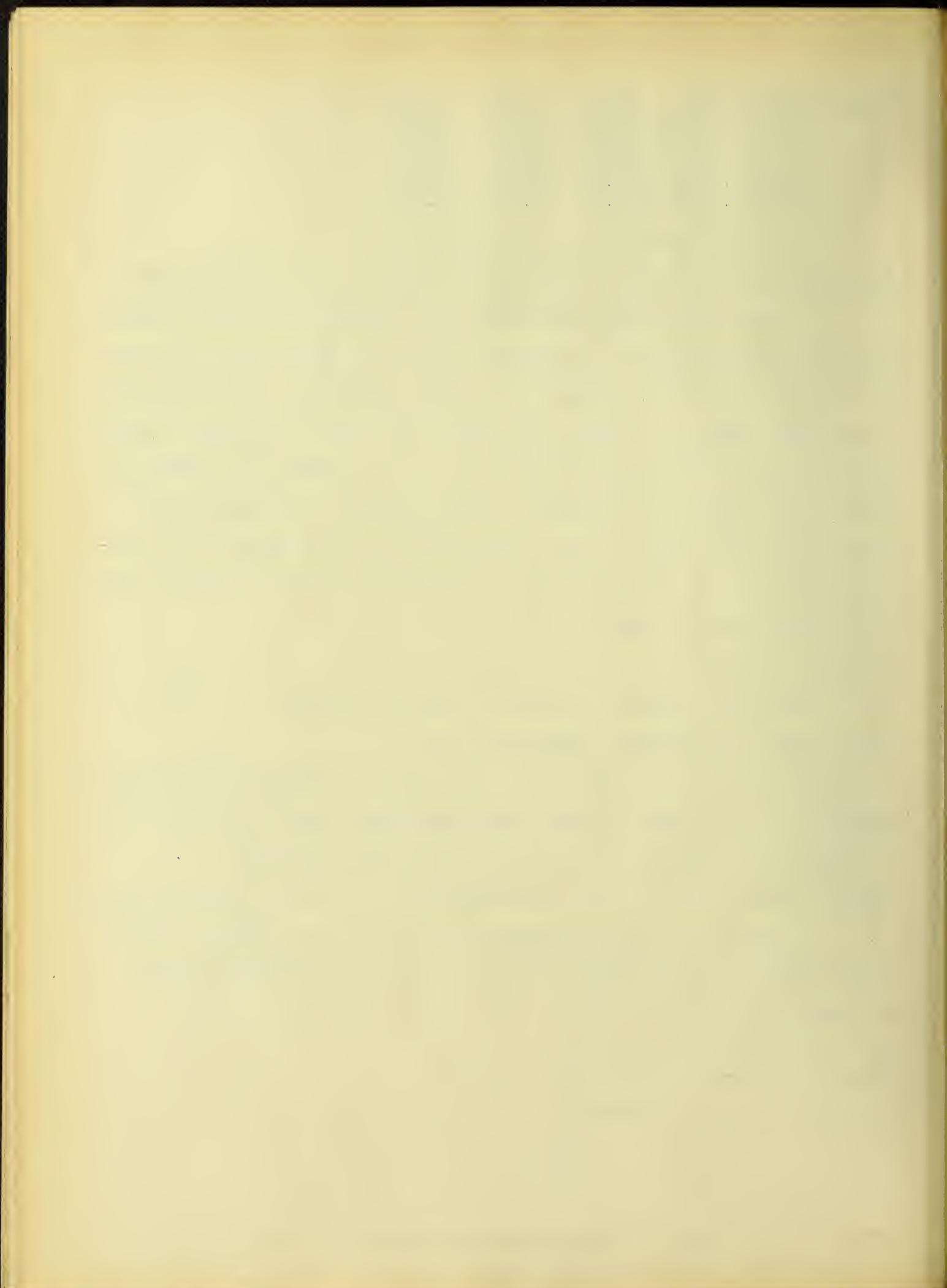
The amount of ferrous salts being determined by titration with permanganate. If only slightly more than theoretical amount of ferric salt is added, the oxidation of hydroxylamine takes place thus-



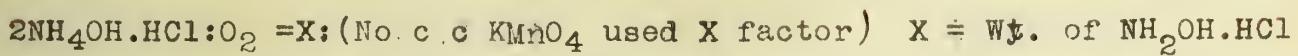
The potassium permanganate used contained .00489 g. available O per c.c., being standardized with ferrous ammonium sulphate and ammonium oxalate.

+Ber. 10, 1940-48

± J. prakt chem. 78, 289-342



| No. of Expt. | Wt. NH ₂ OH.HCl taken | c.c. of KMnO ₄ used found |
|--------------|----------------------------------|--------------------------------------|
| 1 | .1931 g | .1665 78.2 c.c. |
| 2 | .1121 g | .0971 46.95 " |
| 3 | .0737 g | .0559 24.75 " |
| 4 | .1207 g | .0924 43.55 " |
| 5 | .0935 g | .0874 41.25 |



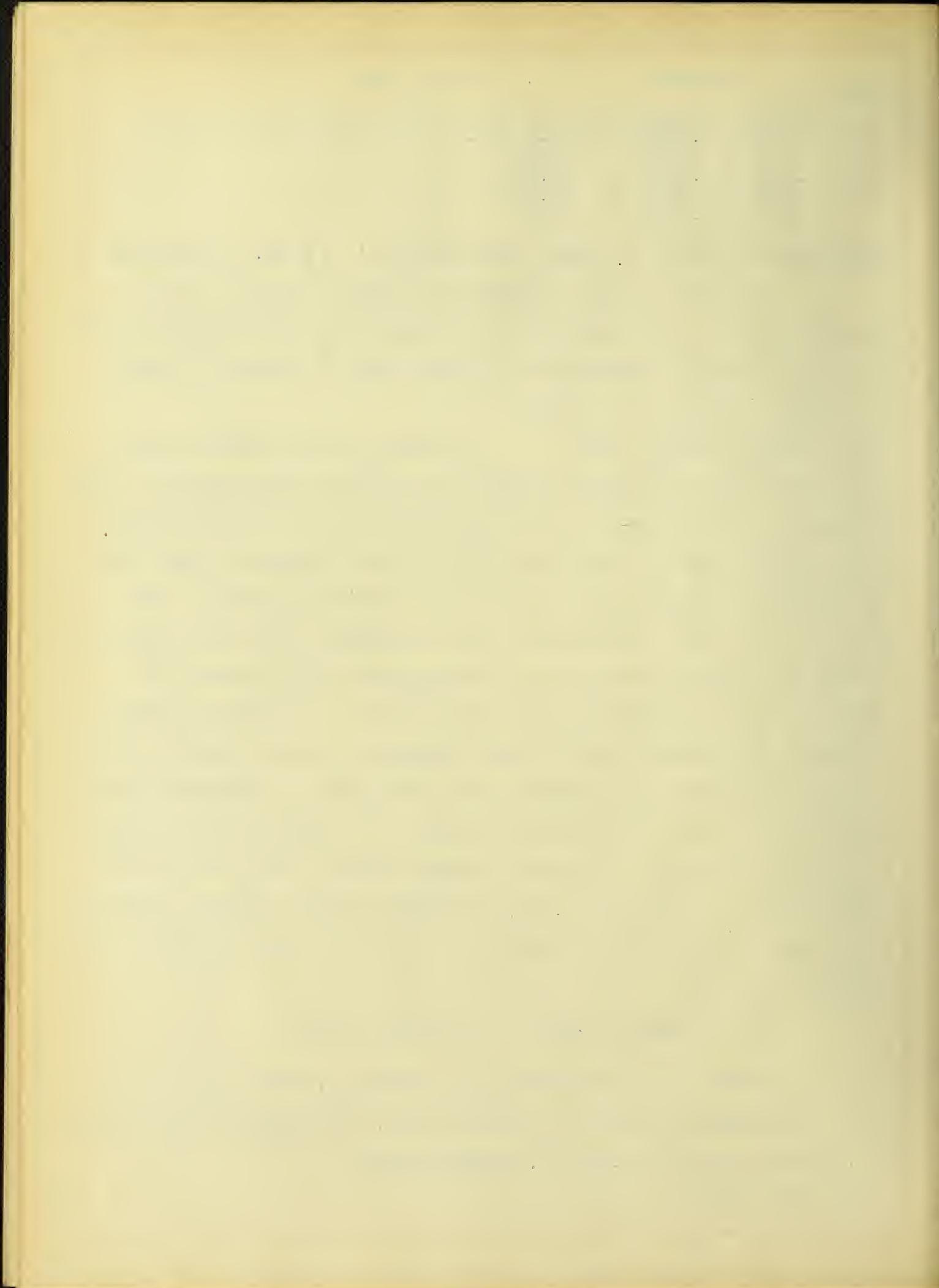
The most accurate quantitative method found and the one used for all the later quantitative estimations of hydroxylamine, was the one of Stähler⁺ where-by the hydroxylamine is reduced by means of titanous sulphate or oxide.

$\text{Ti}_2\text{O}_3 + \text{NH}_2\text{OH} = 2\text{TiO}_2 + \text{NH}_3$ An excess of the titanium solution is used and the excess titrated with standard permanganate. The process is as follows:- To a small weighed portion of hydroxylamine salt, add about 50 c.c. water and allow carbon dioxide to pass into it for several minutes before adding the titanium solution. Let stand for some time to allow it to act, otherwise the action will be between the hydroxylamine and the permanganate, then titrate the excess of titanium solution with permanganate. A decided end point is noted. The titanium solution was prepared by fusing titanium oxide, Ti O₂ with potassium acid sulphate, then dissolving in water acidified with sulphuric acid. The titanium solution is reduced from Ti(SO₄)₂ to Ti₂(SO₄)₃ by means of nascent hydrogen evolved from zinc and sulphuric acid. Permanganate standardized by ferrous ammonium sulphate, 1 c.c. being equivalent to .000234 g O was used to get strength of the titanium solution.

$$1 \text{ c.c. KMnO}_4 = 1.24 \text{ c.c. titanium solution}$$

Since 1 c.c. of permanganate contains .000234 grams of Oxygen, then oxygen required to oxidize 1 c.c. of titanium solution will be .000234 divided by 1.24 or .0001889 grams.

+ Ber. 37, 4732-39



Since -
 $Ti_2(SO_4)_3 + 2NH_2OH + 2H_2SO_4 \xrightarrow{?} Ti(SO_4)_2 + (NH_4)_2SO_4 + H_2O$, one gram molecule of hydroxylamine gives for oxidation sixteen grams of oxygen. $69.5 : 16 = X : (.0001889 \times \text{number of c.c. of titanium solution used})$

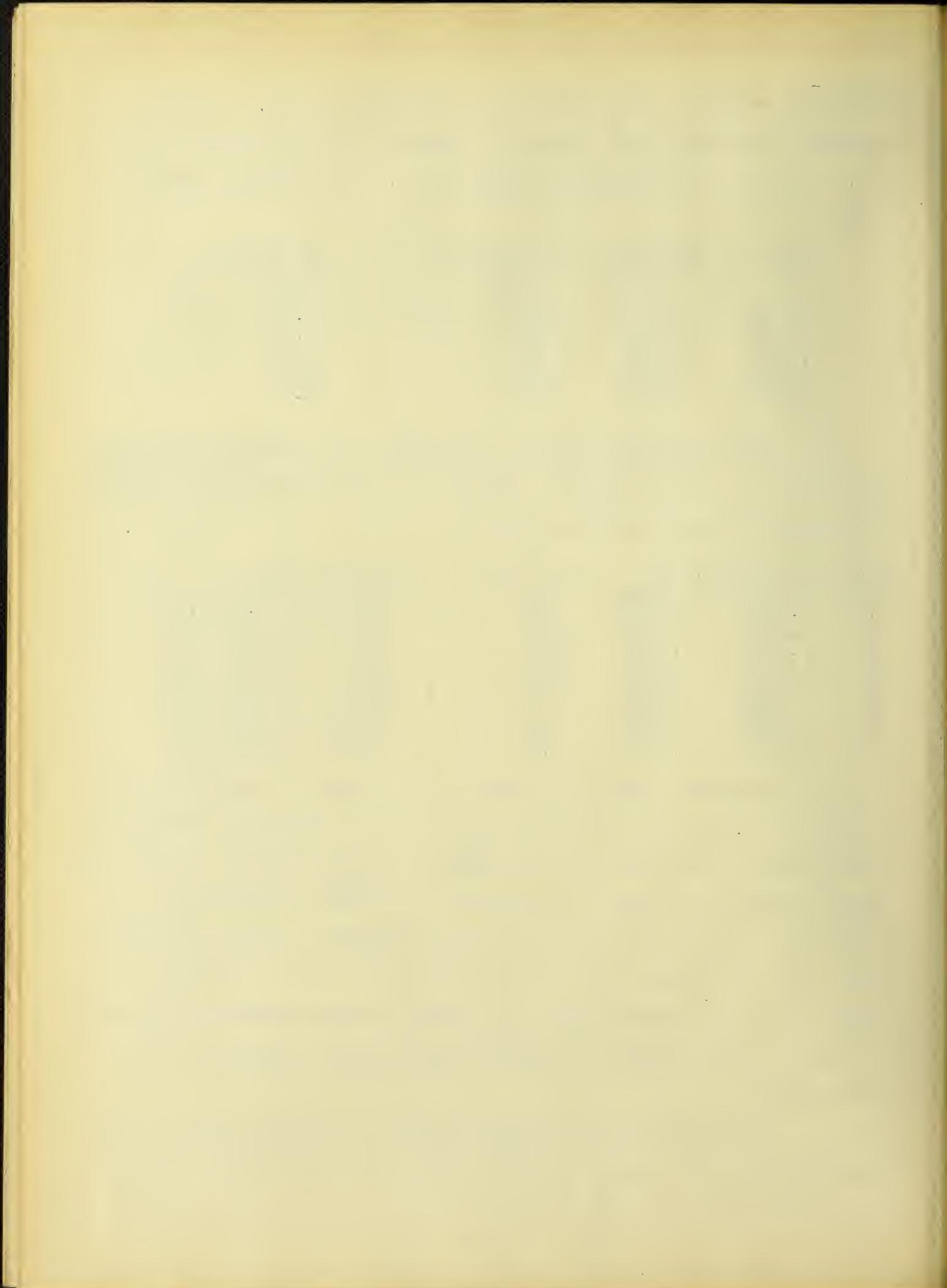
| grams of $NH_2OH \cdot HCl$ used | found | Ti solution taken | c.c. $K Mn O_4$ used |
|-------------------------------------|--------|----------------------|-------------------------|
| .0193 | .01922 | 25 | 1.2 |
| .0055 | .00758 | 10 | .95 |
| .0041 | .00402 | 15 | 7.5 |
| .1695 | .1693 | 210 | 2.5 |
| .0034 | .00342 | 10 | 4.7 |

With titanium solution, of which 1 c.c. requires for oxidation 1.28 c.c. of permanganate equivalent to .000183 grams of oxygen, the following results were obtained:-

| No. of Expt. | g. $NH_2OH \cdot HCl$ taken | C.C. $K Mn O_4$ found | Ti Solution taken | used |
|-----------------|--------------------------------|--------------------------|----------------------|------------|
| 1 | .0171 | .0175 | 25 c.c. | 22.12 c.c. |
| 2 | .0074 | .0072 | 15 c.c. | 9.18 c.c. |
| 3 | .0390 | .0468 | 80 c.c. | 59.01 c.c. |
| 4 | .0254 | .0131 | 50 c.c. | 35.98 c.c. |
| 5 | .0275 | .0264 | 35 c.c. | 33.27 c.c. |
| 6 | .0331 | .0324 | 50.c.c. | 41.02 c.c. |
| 7 | .0340 | .0324 | 45.c.c. | 40.74 c.c. |
| 8 | .0149 | .0145 | 20 c.c. | 18.27 c.c. |

In number three the result is too high and in number four far too low, this error is very likely due to conditions, either the hydroxylamine hydro-chloride and titanium solution did not stand long enough to thoroughly react or an excess of titanium solution was not added and the action was between the permanganate and the hydroxylamine. The best results were obtained when the salt was allowed to react for five minutes or more in a rather strong sulphuric acid solution and in an atmosphere of carbon dioxide before titration with permanganate.

Another method ,not before worked out is the reduction of chromic salts. The reduction was carried out in the absence of ox-

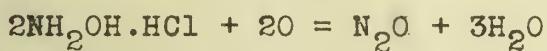


ygen and assumed to be similar to ferric sulphate reduction.

$2\text{Cr}_2(\text{SO}_4)_3 + 2\text{NH}_2\text{OH} = 4\text{CrSO}_4 + 2\text{H}_2\text{SO}_4 + \text{N}_2\text{O} + \text{H}_2\text{O}$, although none of the gases were analyzed. An excess of the chromic salt was added to a weighed amount of the hydroxylamine hydrochloride, then the chromous salt formed was titrated with known permanganate. The hydroxylamine salt and the chromic sulphate were allowed to stand for some time in a carbon dioxide atmosphere, the solution was heated to boiling to drive off the oxides of nitrogen assumed to be present because when the solution is not heated the reduction power is increased very much. This method is simple yet accurate, decided end point being brought out in the green chromate solution by the permanganate.

| No. of Expt. | Wt. NH ₂ OH.HCl taken | Wt. NH ₂ OH.HCl found | c.c. KMnO ₄ used |
|--------------|----------------------------------|----------------------------------|-----------------------------|
| 1 | .0543 g | .0530 g | 10.8 |
| 2 | .1785 g | .1652 g | 33.4 |
| 3 | .0434 g | .0409 g | 8.35 |
| 4 | .1045 g | .1036 g | 21.1 |
| 5 | .0776 g | .0765 g | 15.6 |
| 6 | .0515 g | .0506 g | 10.3 |

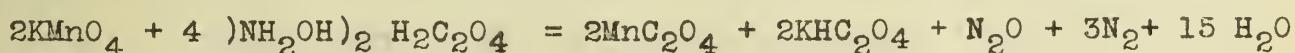
$$1 \text{ c.c. KMnO}_4 = .00113 \text{ g}$$



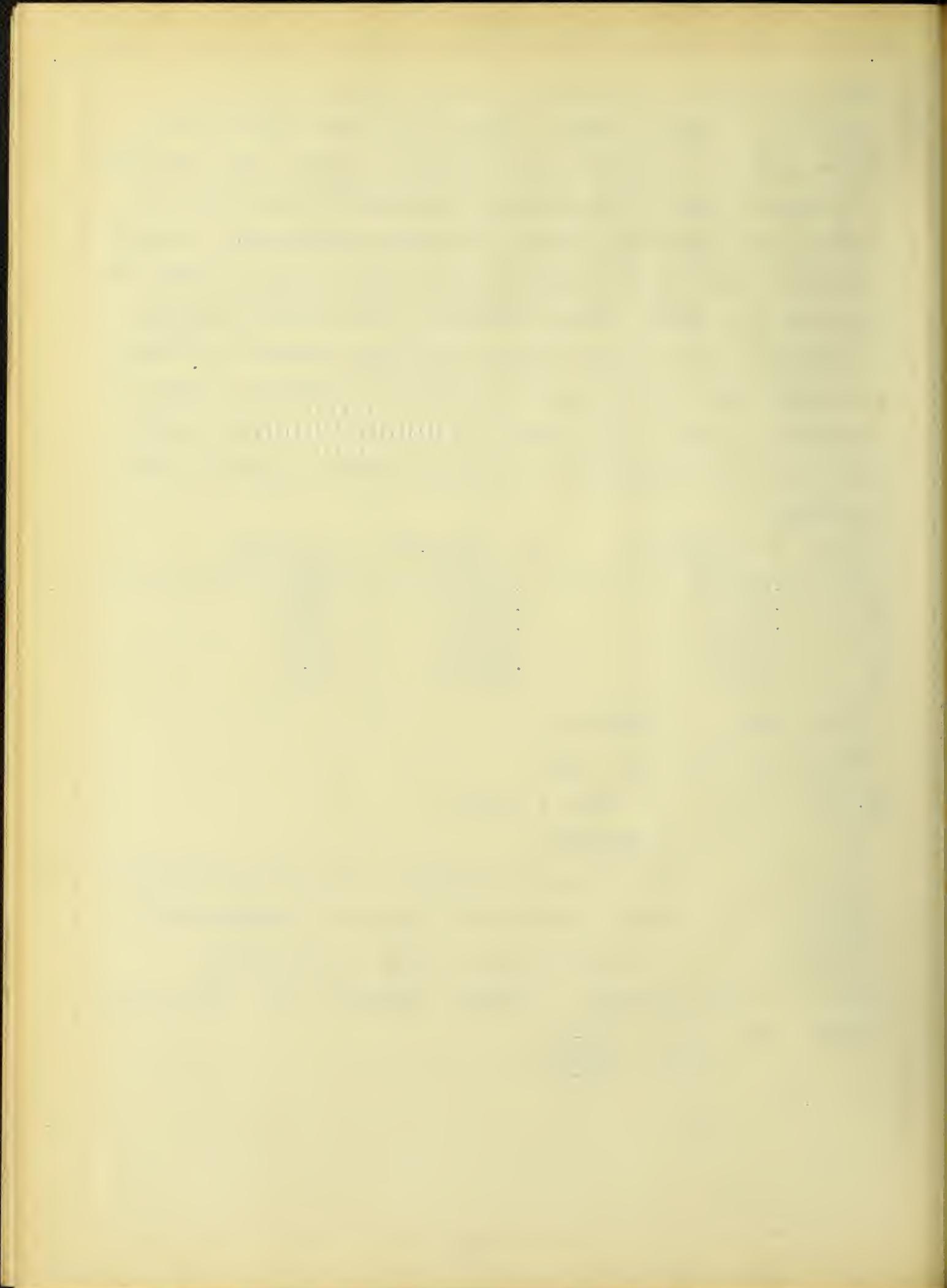
$$69.5:16 = X : (\text{No. c.c. KMnO}_4 \times \text{factor})$$

$$X = \text{Wt. of NH}_2\text{OH.HCl.}$$

+L.J. Simon's volumetric method of determining hydroxylamine salts is by direct titration with potassium permanganate in neutral solution. The hydroxylamine alone, being oxidized



+ Compt. rend. 135, 1339-42
140, 659-661
140, 724-27



One molecule of permanganate oxidizes four molecules of hydroxylamine. In presence of oxalic acid, the acid is oxidized. The oxidation of the sulphate is as follows:-



If sulphuric acid is added, the nitrite is oxidized. The reducing power is increased if the solution is but slightly acid. The accuracy also depends upon the temperature and the rate of titration.

Owing to the varying reducing effects of the acid with which the hydroxylamine is combined, better results are obtained if an equivalent amount of sodium oxalate is added to the solution of hydrochloride, nitrate or sulphate of hydroxylamine. Then the mixture behaves as if it were pure hydroxylamine oxalate and can be titrated exactly with permanganate. The results are not effected if there is an excess of oxalic acid. Slightly abnormal results are obtained when the quantity of sodium oxalate in excess of the theory is very small, due to its action in reducing the hydroxylamine oxalate. The following were done with hydroxylamine in presence of sodium oxalate.

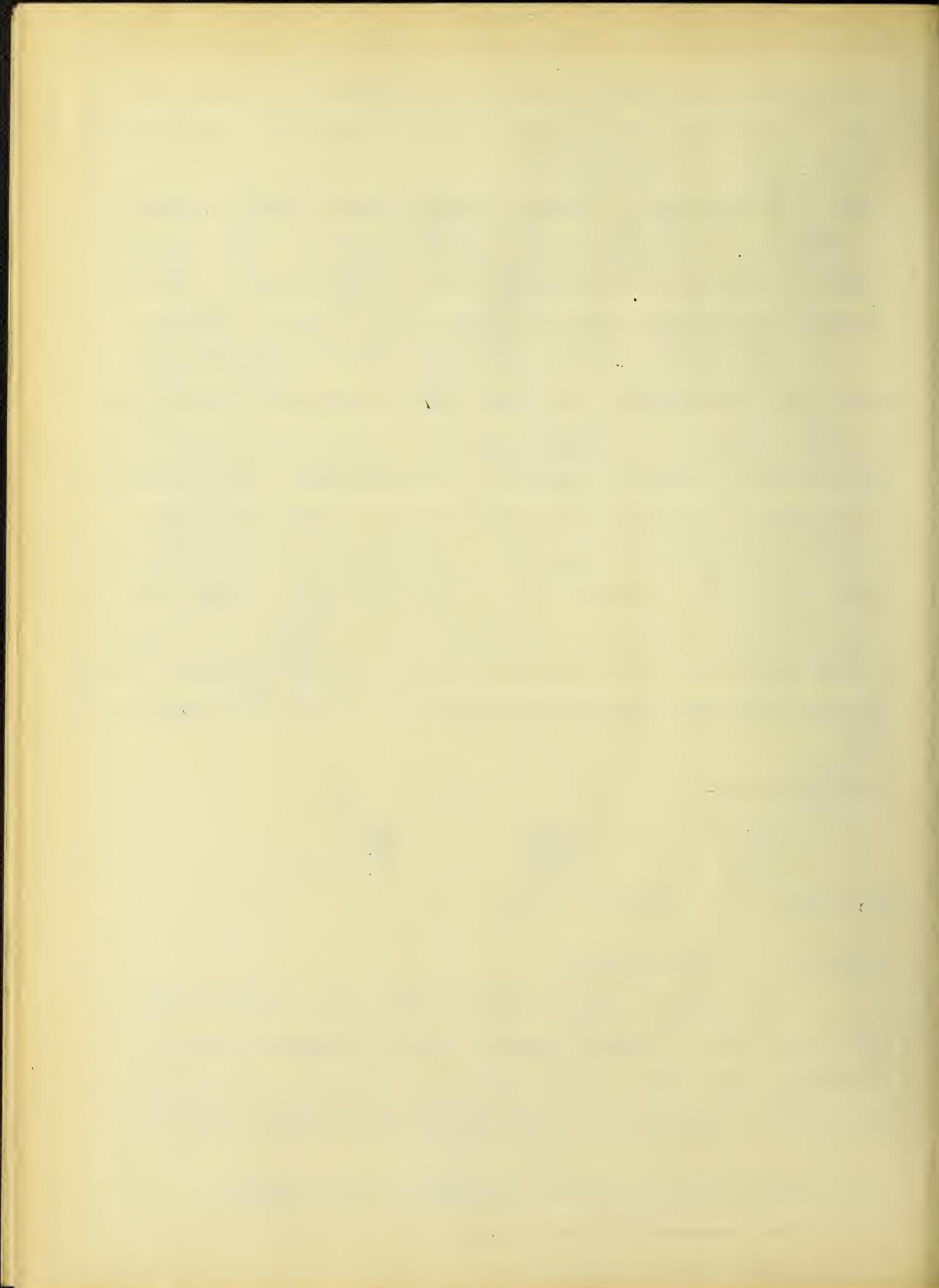
| grams $\text{NH}_2\text{OH} \cdot \text{HCl}$ - | c.c. of KMnO_4 |
|---|-------------------------|
| used- | found |
| .2697g. | .1534g. |
| .1766g. | .1171g. |
| | used |
| | 31.25 c.c. |
| | 21.10 c.c. |

1 c.c. KMnO_4 = $\frac{1}{5}$.000113 g. oxygen.

Double Salts of Hydroxylamine.

Many double salts of hydroxylamine have already been prepared, some done in aqueous solution and many containing water of crystallization. Some of the double salts formed in this manner are as follows:- ⁺ Compounds of hydroxylamine with metallic carbonates:

⁺Zeit. anorg. Chem. 5, 129-46 By Goldschmidt and Syngros.



Di-hydroxylamine zinc carbonate $Zn(NH_3O)_2CO_3$ a white, micro-crystalline powder, insoluble in water.

Manganese chloride mixed with sodium carbonate and hydroxylamine hydrochloride gives a white precipitate of $4MnCO_3 \cdot 3NH_3O \cdot 2H_2O$.

A similar compound is formed with cobalt.

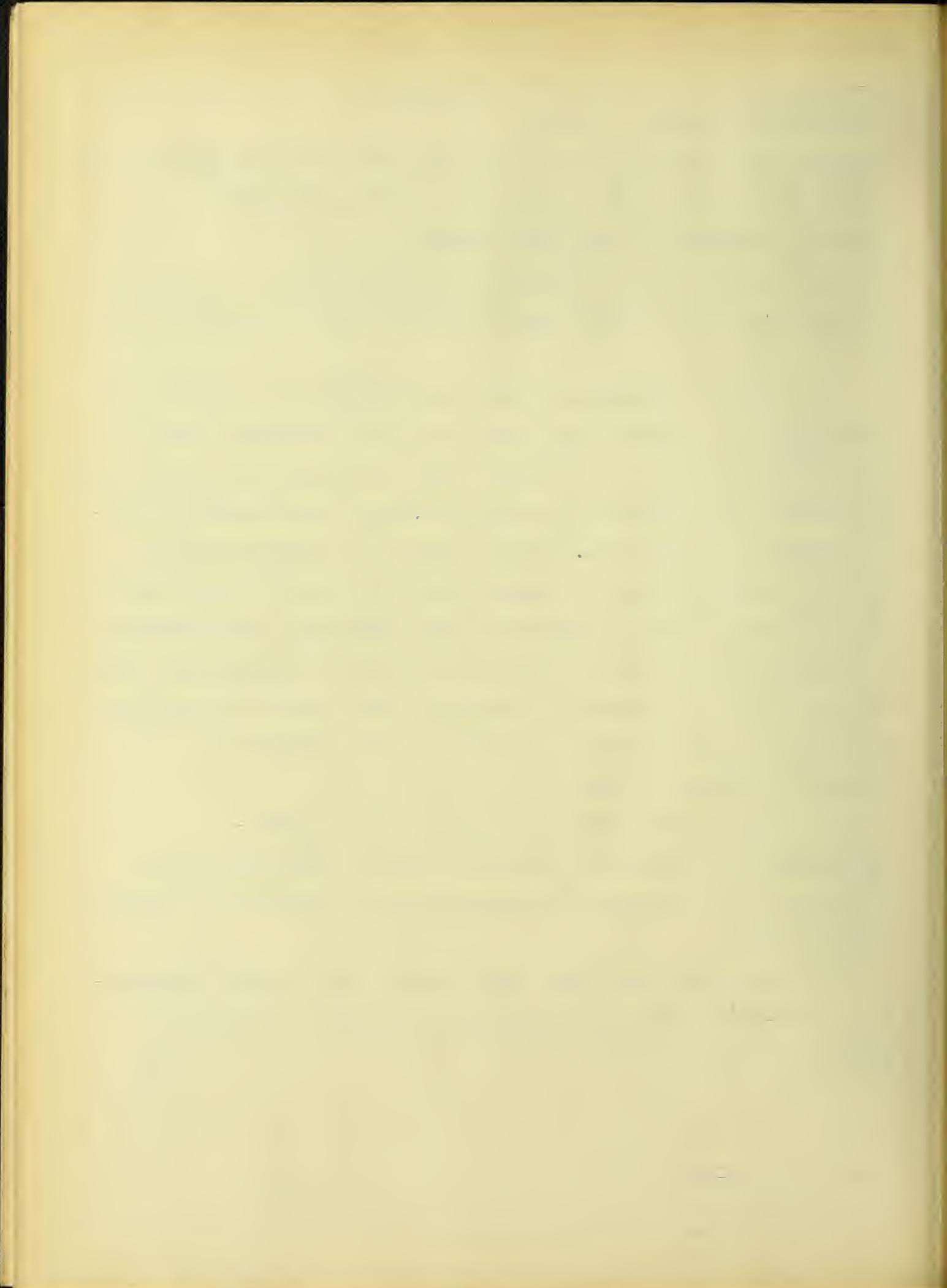
Cadmium chloride forms a double salt with hydroxylamine of formula $(Cd(NH_3O)_2Cl_2)$ which crystallizes in white prisms of sp.gr. 2.72 at 18° .

Several compounds of cobalt are known, +the compound $CoCl_2 \cdot 2NH_3O$ is in form of pink crystals, which decompose readily with the formation of nitrous acid. When the crystals are heated they give ammonia and ammonium chloride. $CoOCl \cdot 2NH_3O$ is an unstable insoluble substance, obtained by passing oxygen at a reduced pressure into an alkaline solution of cobaltic chloride and free hydroxylamine. Yellow crystals of $CoCl_3 \cdot 6NH_2OH$ are formed when the second compound is suspended in alcohol and treated with alcoholic hydrochloric acid. Acidified water or concentrated sulphuric acid dissolves these crystals without decomposition. An oxalate of the formula $Co_2(C_2O_4)_3 \cdot 12NH_3O$ is known.

Copper forms compounds similar to the cobalt-- $CuSO_4 \cdot NH_3O \cdot 2H_2O$, soluble in hot water, but not dissolved by cold. An oxidation of the crystals is accompanied by formation of a stable, brown product.

Manganese forms very stable salts-- $MnCl_2 \cdot 2NH_3O$, decomposing at $150-160^\circ$. $MnSO_4 \cdot NH_3O \cdot 2H_2O$, a white powder, insoluble in water.

+ Ber. 27, 401-406.



+Kohlschutter prepared the compounds-- HO-Ca-ONH_2 from lime and hydroxylamine, a white powder and a strong reducing agent.

$\text{NH}_4\text{O}\cdot\text{WO}_4\cdot\text{NH}_4$, a tungstate, giving thick crystalline tablets.

$\text{NH}_4\cdot\text{HPO}_3\cdot\text{NH}_4\text{O}$, white needle-like crystals

$\text{HPO}_3(\text{NH}_4)_2$, colorless needles, which when heated burn with a green flame and evolve hydrogen phosphide.

$(\text{H}_2\text{PO}_2)_2(\text{NH}_3\text{O})_3\text{K}_2$, thin plates which melt at 86° and are easily soluble in water at 90° .

The first phosphorus salt is obtained from phosphoric acid, and the second from disodium phosphite.

Metavanadic acid VO_3H yields three crystalline products--

$\text{VO}_3\text{H}(\text{NH}_3\text{O})_3$, $\text{VO}_3\text{H}(\text{NH}_3\text{O})_3(\text{NH}_3)_2$, $\text{VO}_3\text{H}(\text{NH}_3\text{O})_2(\text{NH}_3)_2$

The first two separate out in lemon yellow crystals, the third cannot be obtained in the pure state.

The neodymium compound $\text{NbO}_3\text{H}(\text{NH}_3\text{O})_3$ is a white powder slightly soluble in water and explodes with a yellow flame when heated.

+ Uhlenhuth prepared the following compounds--

$\text{NiSO}_4\cdot 6\text{NH}_2\text{OH}$, red, quadratic crystals which belong to the triclinic system, the figures and measurements being given.

$\text{Pt}(\text{NH}_2\text{OH})_4(\text{OH})_2$, snow white crystals, insoluble in alcohol or ether but readily soluble in mineral acids. Nitric acid decomposes the crystals.

$\text{Pt}(\text{NH}_2\text{OH})_4\text{SO}_4$, large triclinic crystals.

$\text{Pt}(\text{NH}_2\text{OH})_4\text{Cl}_2$, flat needles.

$\text{Pt}(\text{NH}_2\text{OH})_2\text{Cl}$, a yellow salt.

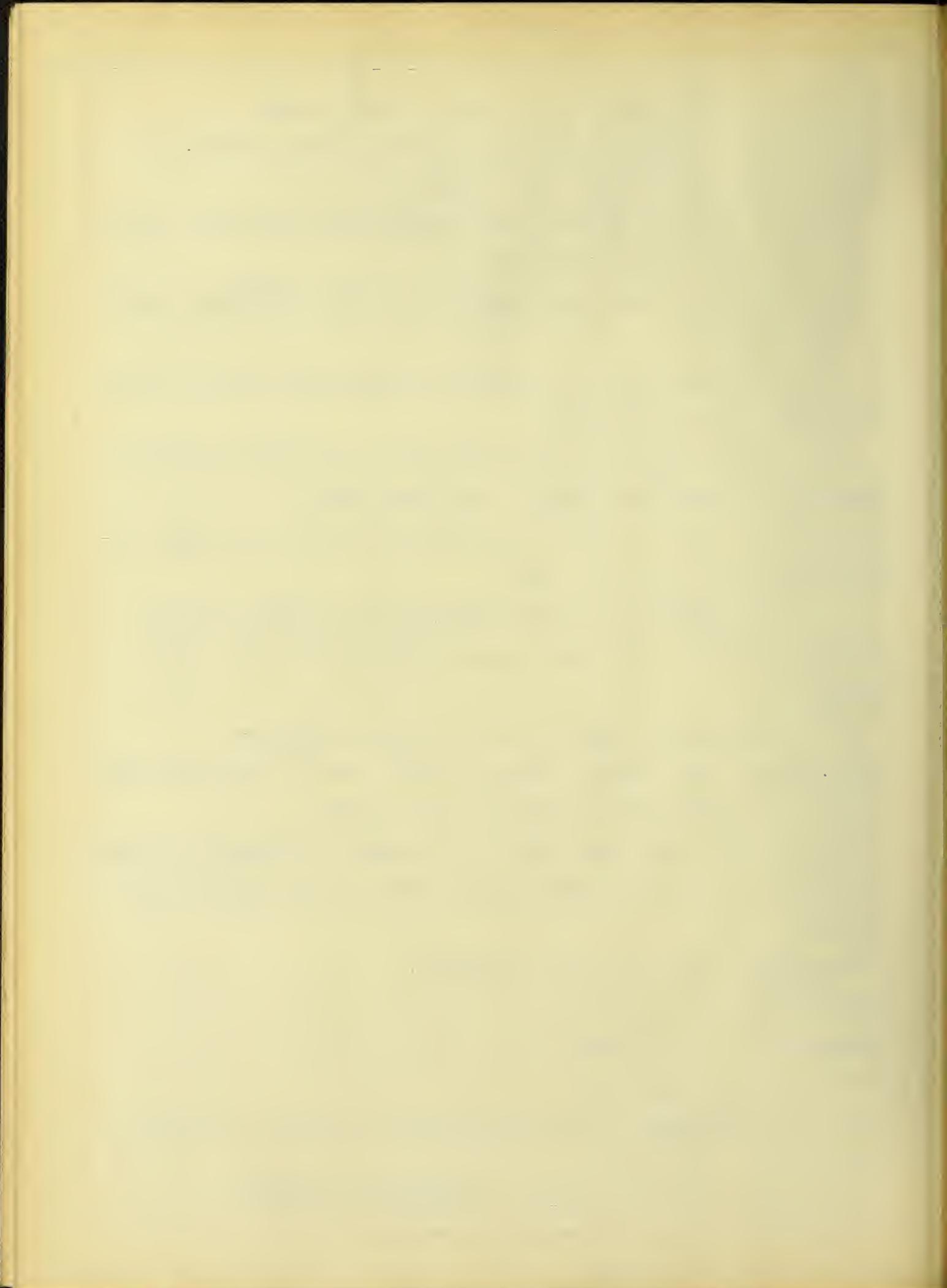
$\text{Pt}(\text{NH}_2\text{OH})_2\text{Cl}_2$, a blue salt.

$(\text{NH}_2\text{OH})_2\text{H}_2\text{Pt}(\text{CN})_4\cdot 2\text{H}_2\text{O}$, soluble red crystals, stable at ordinary temperatures.

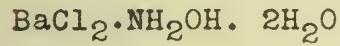
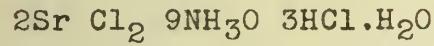
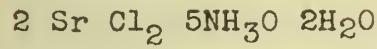
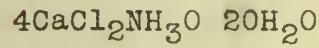
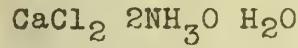
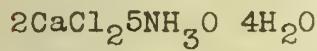
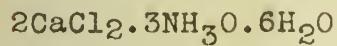
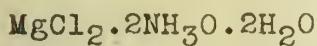
+Annalen 307, 332-334

+ Zeit. anorg. Chem. 16, 463-74

+ Annalen 311, 127-28



+ Antonoff gives the compounds of haloid salts of metals with hydroxylamine as follows obtained from aqueous alcoholic solution.



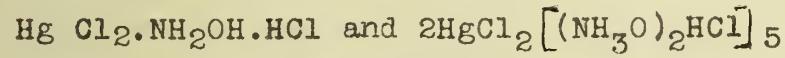
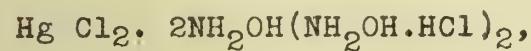
An aqueous solution saturated at 20° contains about one percent $\text{CdCl}_2 \cdot 2\text{NH}_2\text{OH}$, 44.4% of $\text{MgCl}_2 \cdot 2\text{NH}_3\text{O} \cdot 2\text{H}_2\text{O}$ and about 56.6% of $\text{CaCl}_2 \cdot 2\text{NH}_2\text{OH} \cdot \text{H}_2\text{O}$.

+ Maxwell Adams prepared the following salts--

$\text{NH}_2\text{OH} \cdot \text{HBr}$, large white crystals, which are very soluble in water,

$2\text{NH}_2\text{OH} \cdot \text{HBr}$ white plates,

mercuric chloride combines with hydroxylamine hydrochloride to form



The bromide $\text{Hg Br}_2 \cdot 2\text{NH}_3\text{O} (\text{NH}_3\text{O} \cdot \text{HBr})_2$ and the bromide of cadmium

$\text{Cd Br}_2 \cdot 2\text{NH}_3\text{O}$ and $\text{Cd F}_2 \cdot 3\text{NH}_3\text{O}$ are also formed.

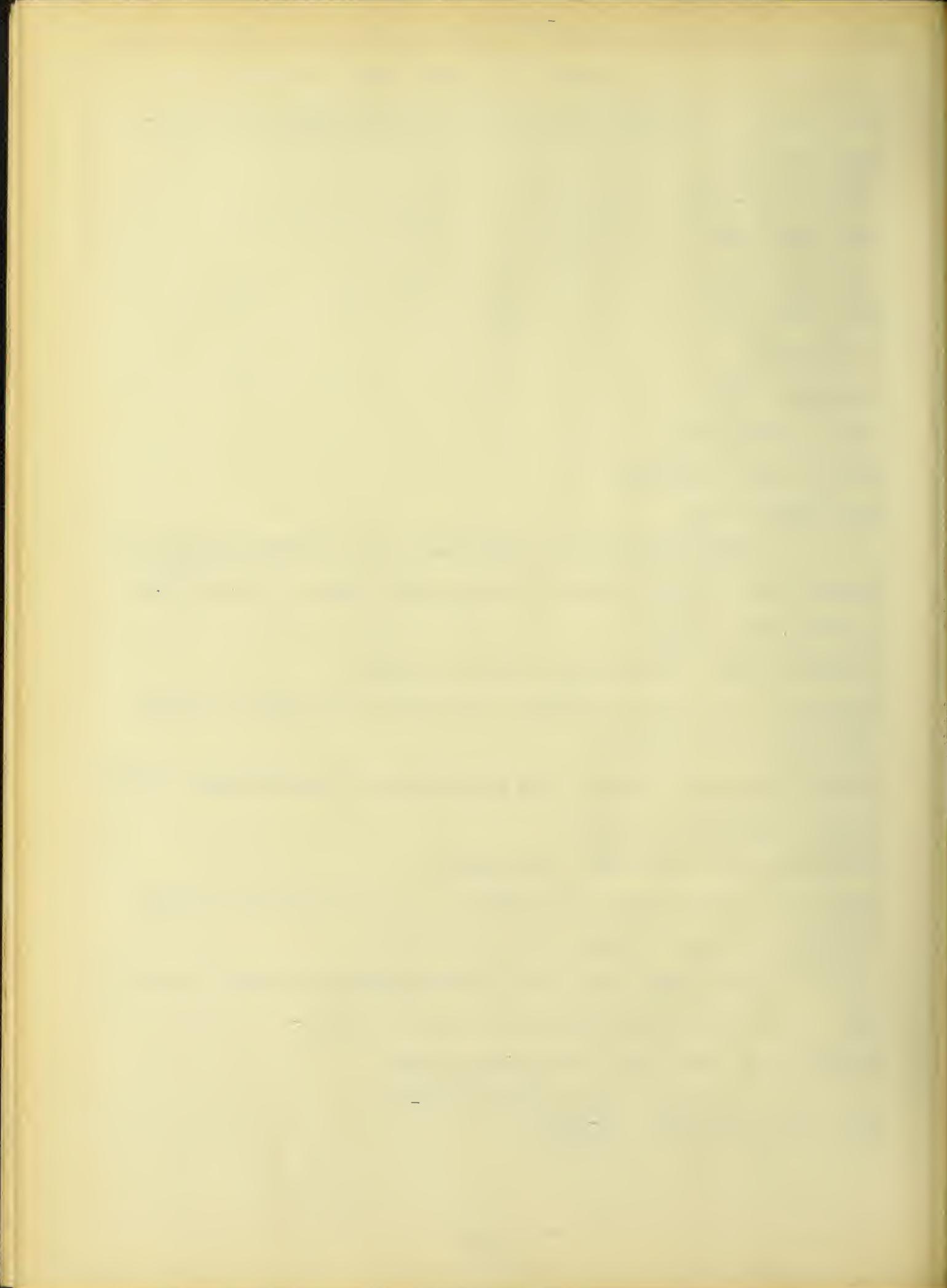
+ W.H. Ross found that hydroxyl ammonium sulphate melts at 163° with decomposition and breaks up as follows:-



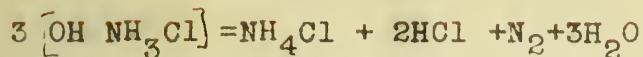
+ Jour. Russian Phys. Chem. Soc. 37, 476-83

+ Am. Chem. Jour. 28, 198-219

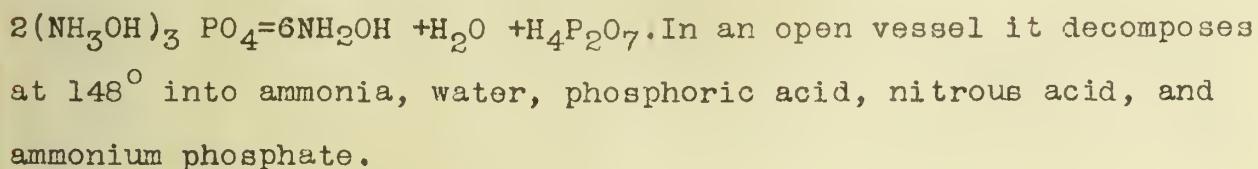
+ Jour. Chem. Soc. Ab. 1906, 19



The chloride melts at 157° , decomposes according to --



The phosphate is only slightly soluble in cold water but readily forms supersaturated solutions. When heated in a vacuum, it decomposes according to --

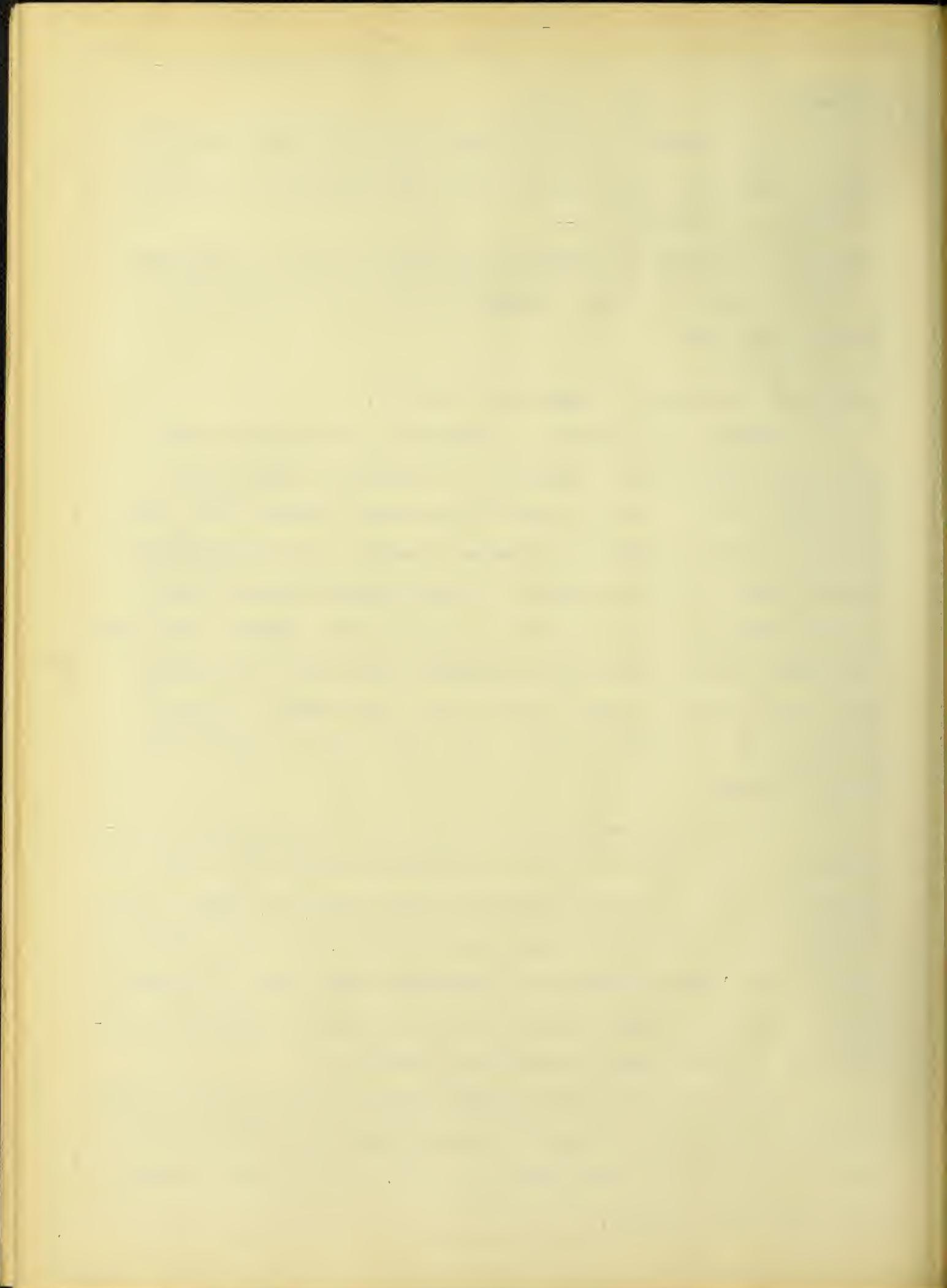


Salts of hydroxylamine in anhydrous solution.

None of the preceding experiments, from which double salts were obtained, were carried on in anhydrous solution, and the object now, is to see if salts like copper sulphate will crystallize with hydroxylamine in absence of water. As the hydroxylamine was found to be more stable in methyl alcohol than in ethyl alcohol, absolute methyl alcohol was used as the solvent. The absolute methyl alcohol after being boiled several days with calcium oxide, and allowed to stand several hours over metallic calcium, was distilled and tightly corked. The ether used was dried over calcium chloride.

The weighed amount, about 10 grams, of hydroxylamine hydrochloride was dissolved in 60 c.c. of absolute alcohol and then the calculated amount of freshly prepared sodium methylate added. Ether was now added to precipitate the sodium chloride and the clear solution of free hydroxylamine was filtered off and used to dissolve metallic salts, as copper sulphate, nickle sulphate, manganese chloride etc. In every case the salts were anhydrous.

Using ten grams hydroxylamine hydrochloride would be about the same as adding five grams free hydroxylamine and making up to about one hundred and twenty-five c.c., the solution would contain about .04 grams per c.c.



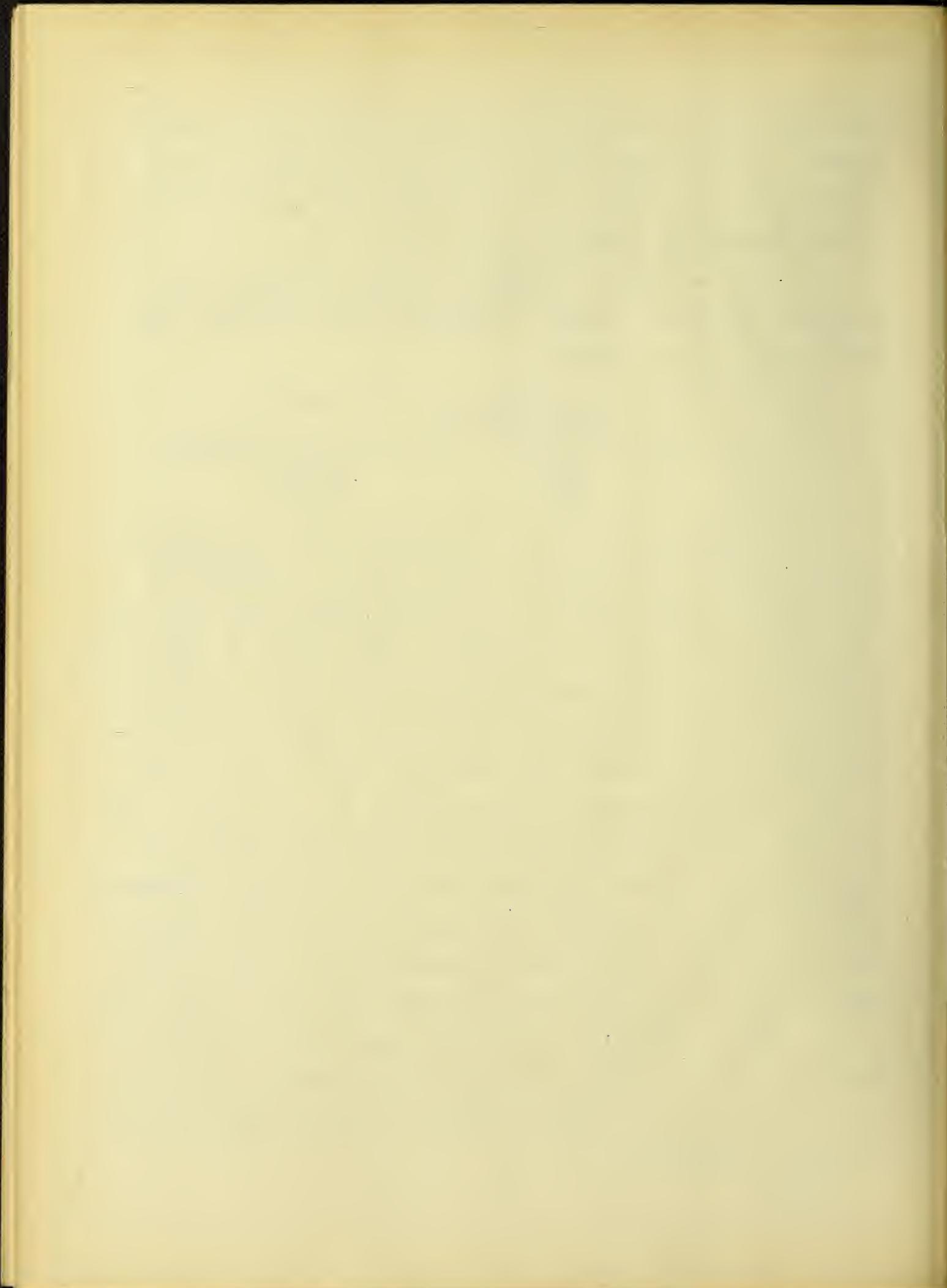
In trying to determine amount of hydroxylamine in solution with titanium solution, no concordant results were obtained, .000464, .000234, .00053 grams respectively. No reason has yet been found why the titanium would not react quantitatively with the hydroxylamine in alcohol solution.

But the method of reduction of ferric sulphate worked accurately enough for strength of solution giving .0433 and .0471 grams per c.c. of the solution.

| c.c. of NH ₂ OH sol. used. | c.c. KMnO ₄ used to oxidize the FeSO ₄ | Wt. NH ₂ OH per c.c. solution |
|--|--|---|
| 10 | 69.3 | .0433 g. |
| 20 | 192.8 | .0471 g. |

Knowing approximately the strength of the hydroxylamine solution, and allowing an excess over the amount to crystallize with anhydrous copper sulphate to form CuSO₄.6NH₂OH, the green solution (obtained by allowing the alcoholic hydroxylamine to stand over anhydrous copper sulphate) was filtered and allowed to crystallize in a quiet room at a temperature below fifteen degrees. The crystals came down very slowly, some taking two weeks or over. They are very easily decomposed as soon as brought into the air, so that great care and haste has to be taken in successfully getting the crystals out of the solution, dried, and the hydroxylamine determined before the crystals decompose. The copper crystals were beautiful green, transparent crystals, but in decomposing they left a white powder in every way similar to the anhydrous salt used to start with.

It was found that the crystals came down sooner from a more saturated solution, gotten by allowing the hydroxylamine solution to stand over the anhydrous copper sulphate for several days, then filtering and crystallizing.



were

The crystals taken from the solution dried on filter paper and a porous plate and poured into a weighed tube. The portions for analysis were weighed by difference and the work done as rapidly as possible. The hydroxylamine being determined by Stahler's method-- Add an excess of titanium solution and titrate the excess with standard permanganate. Care must be taken to allow time for titanium and hydroxylamine to act else the reaction will be between hydroxylamine and permanganate which is far from quantitative.

+ The copper in the crystals was determined electrolytically according to the method of Smith. The solution is placed in a clean weighed platinum dish and acidified with a few drops of nitric acid, and then electrolysed with a current of .09 amphere and 1.9 volts for four to five hours. At the end of that time the liquid is tested to see if copper is all precipitated. If so, the acid solution is siphoned off and the precipitate of metallic copper washed with hot water and then alcohol. Dry below 100° and weigh when cool. As the strength of the titanium solution changes when standing, its strength had to be found each time by titration with permanganate. The permanganate is $\frac{1}{V} = .000113$ g. O per c.c.

The following results were obtained, numbers 3 and 4 were from the same sample of crystals.

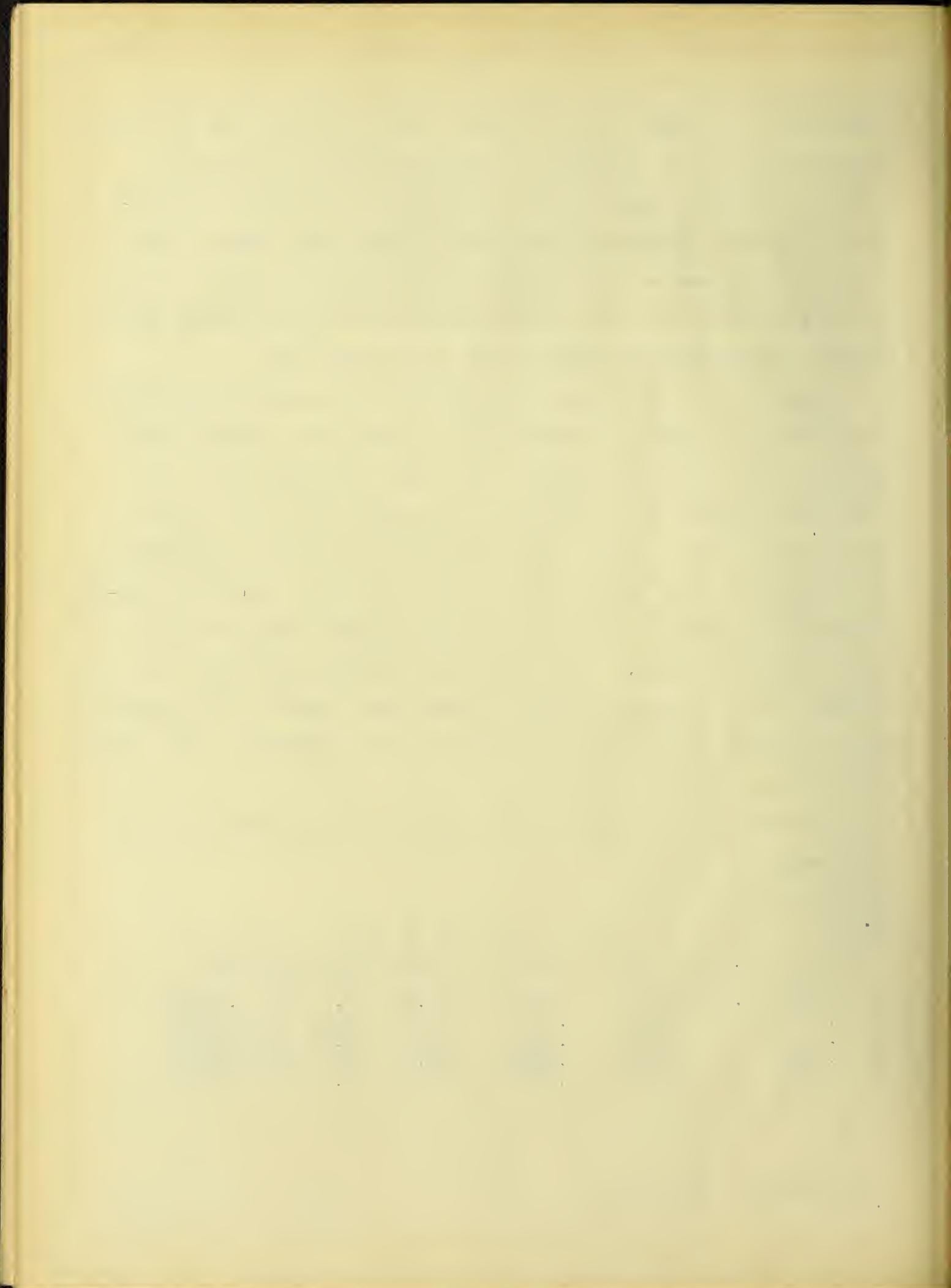
Determination of copper.

No. of

Expt. Wt. in g. Wt. Cu⁺ in g. % of CuSO₄ formula of
Cryst. taken found CuSO₄ theory found compound

| | | | | | | |
|---|-------|-------|-------|-------|-------|--|
| 1 | .5596 | .1367 | .3430 | 61.69 | 61.3 | CuSO ₄ .3NH ₂ OH |
| 2 | .0385 | .0129 | .0323 | 82.79 | 83.89 | CuSO ₄ .NH ₂ OH |
| 3 | .1002 | .0331 | .0828 | 82.79 | 82.63 | CuSO ₄ .NH ₂ OH |
| 4 | .0708 | .0235 | .0586 | 82.79 | 82.77 | CuSO ₄ .NH ₂ OH |
| 5 | .2205 | .0543 | .1362 | 61.69 | 61.77 | CuSO ₄ .3NH ₂ OH |

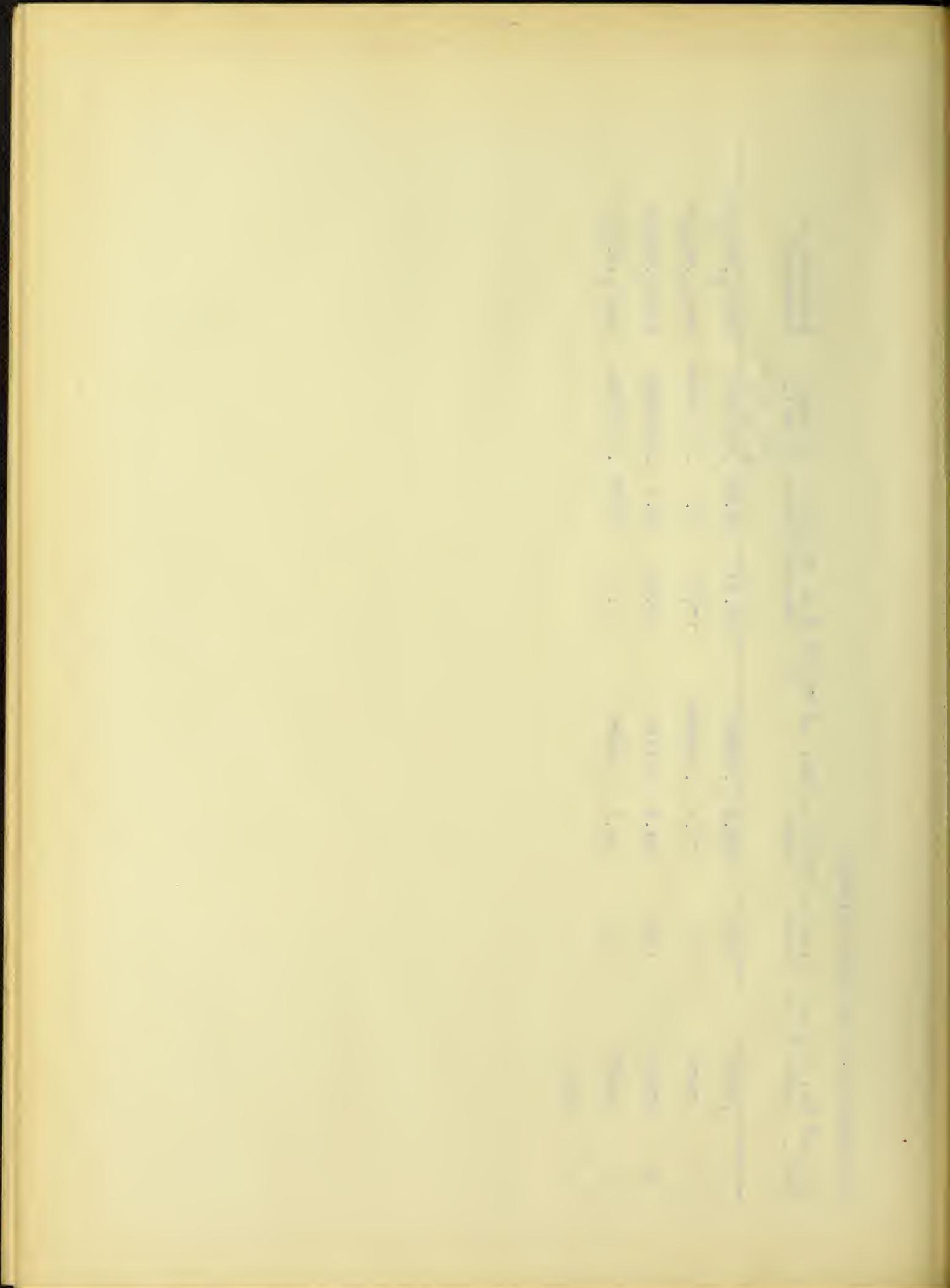
+Smith Electro Chem. 58



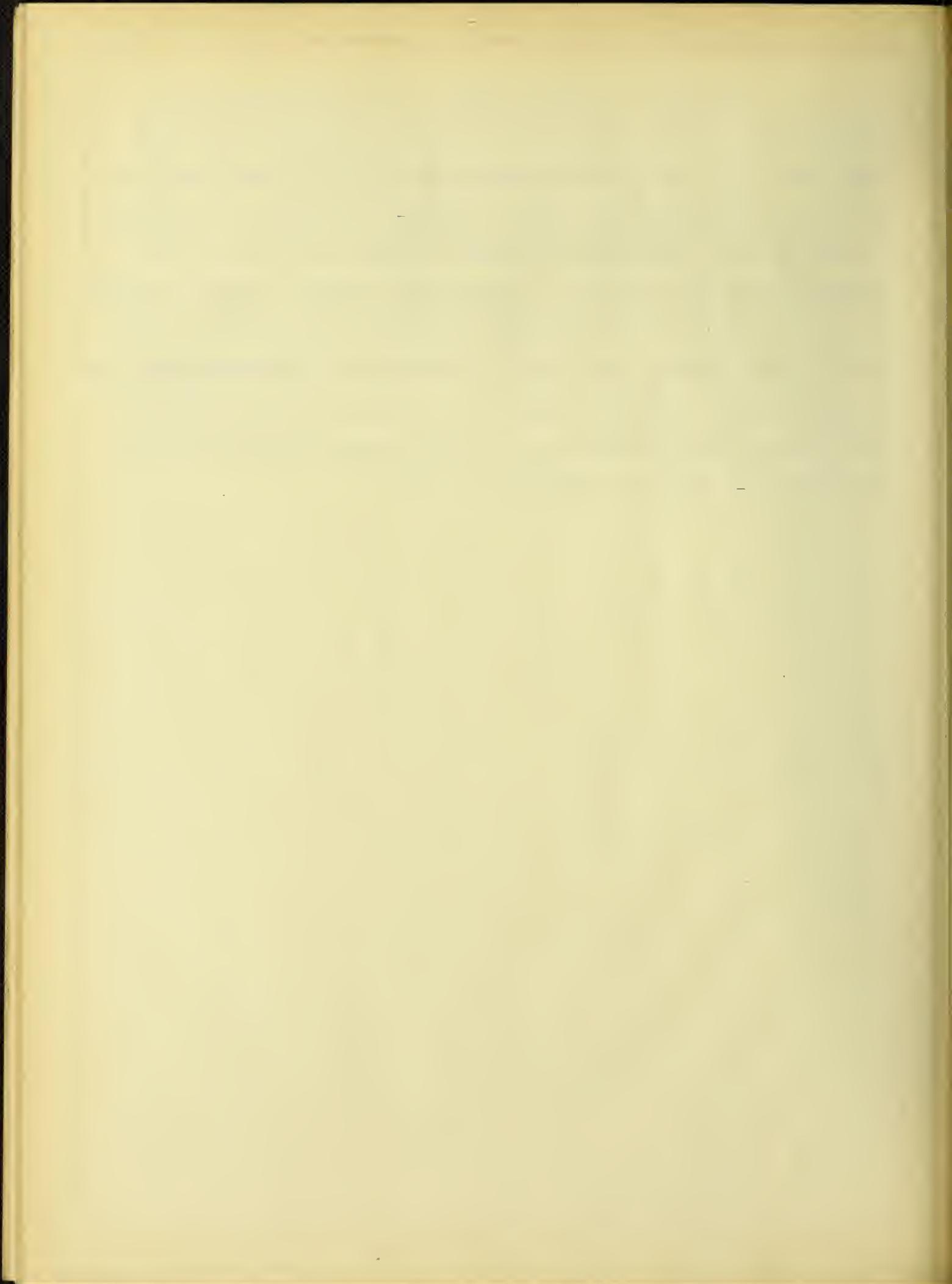
Determination of hydroxylamine

No. of Wt. Crys. c.c. of Ti Sol. Wt. of NH_2OH % of NH_2OH theory found % of NH_2OH Strength per cc in Expt. taken in G. taken used

| | | | | | | | Formula of Compound |
|---|-------|-----|-------|---------|-------|-------|---|
| | | | | | | | g. of O |
| 1 | .0821 | 300 | 206.9 | .03315 | 38.31 | 40.27 | .0000777 CuSO ₄ ·3NH ₂ OH |
| 2 | .0372 | 100 | 75.4 | .006203 | 17.21 | 16.7 | .00003989 CuSO ₄ ·NH ₂ OH |
| 3 | .0691 | 100 | 64.3 | .01198 | 17.21 | 17.5 | .0000904 CuSO ₄ ·NH ₂ OH |
| 4 | .0537 | 100 | 50.1 | .00932 | 17.21 | 17.31 | .0000904 CuSO ₄ ·NH ₂ OH |
| 5 | lost- | -- | | | | | |



Crystals of nickle sulphate with hydroxylamine were obtained in a similar manner to the copper crystals, but in much less time. The hydroxylamine was determined in the same way, the nickle by electrolysis according to Smith--To 50 c.c. of a solution containing about one-tenth of a gram of nickle, add 100 c.c. of ammonium hydroxide and 10 c.c. of ammonium sulphate and use a current of .5 to .7 amperes and 2.8 to 3.3 volts for 3 or 4 hours. At the end of that time test the solution with potassium sulphocarbonate and if only a faint rose color appears the precipitation is complete. The following results were obtained with nickle crystals with hydroxylamine; - $KMnO_4 = \text{?} = .000113$ g. 0 per c.c.

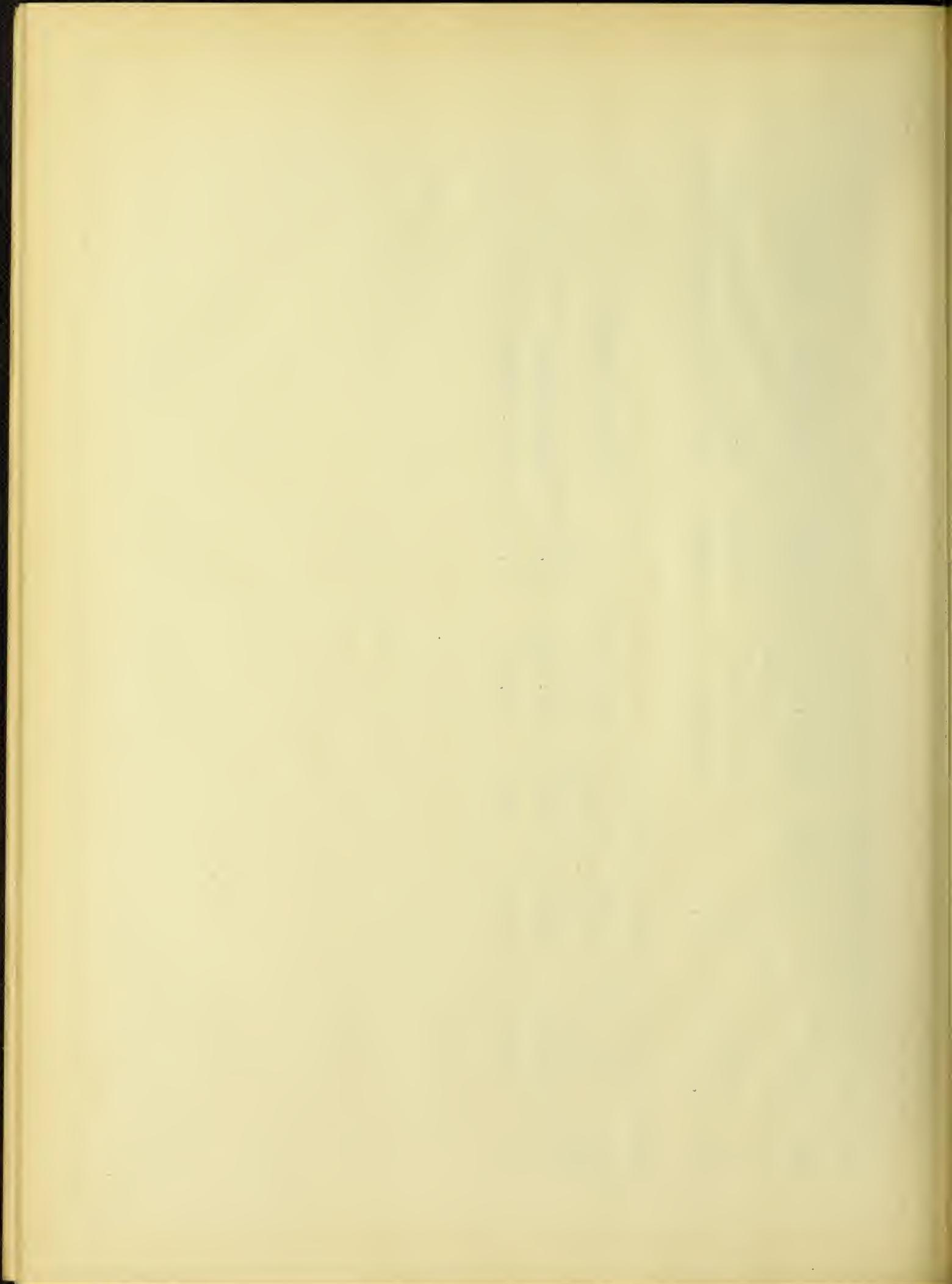


Determinations of hydroxylamine

| No. of Expt. | Wt. crys. | c.c. Ti solution used | Strength Tl Sol. per c.c. | Wt. NH ₂ OH found | % of NH ₂ OH theory found | Formula of Compound |
|--------------|-----------|-----------------------|---------------------------|------------------------------|--------------------------------------|---|
| 1 | .0155 g. | 26.9 | .0001244 g.0 | .0069 g. | 46.09 % | 44.52% NiSO ₄ ·4NH ₂ OH |
| 2 | .0113 g. | 16.8 | .0001828 g. 0 | .00633 | 56.22 % | 57.7 % NiSO ₄ ·6NH ₂ OH |

Determination of nickel in crystals

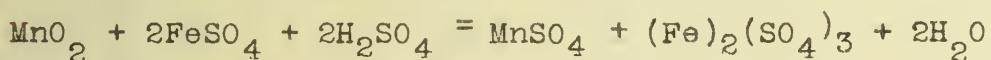
| No. of Expt. | Wt. Crys. | Wt. Ni found, = g NiSO ₄ | % of NiSO ₄ theory found | % of NiSO ₄ found | Formula Compound |
|--------------|-----------|-------------------------------------|-------------------------------------|------------------------------|--|
| 1 | .1013 g. | .0209 g. | .0550 g. | 53.91 % | 54.29 % NiSO ₄ ·4NH ₂ OH |
| 2 | .0753 g. | .0128 g. | .0337 g. | 43.78 % | 44.75 % NiSO ₄ ·6NH ₂ OH |



The easiest and best crystals prepared were the long transparent, pink needles prepared by treating anhydrous manganese chloride with hydroxylamine in absolute methyl alcohol solution. These were fairly stable crystals. Analysis No. 4 is upon the same crystals as No. 2, but two weeks later, the crystals being kept in a calcium chloride desiccator in a glass stoppered bottle.

The hydroxylamine was found by titration with titanium solution and the manganese by adding bromine water in excess and let stand for an hour, then heat to drive off excess of bromine. Add an excess of ferrous sulphate and titrate the excess with permanganate.

One molecule of MnO_2 oxidizes two molecules of $FeSO_4$.



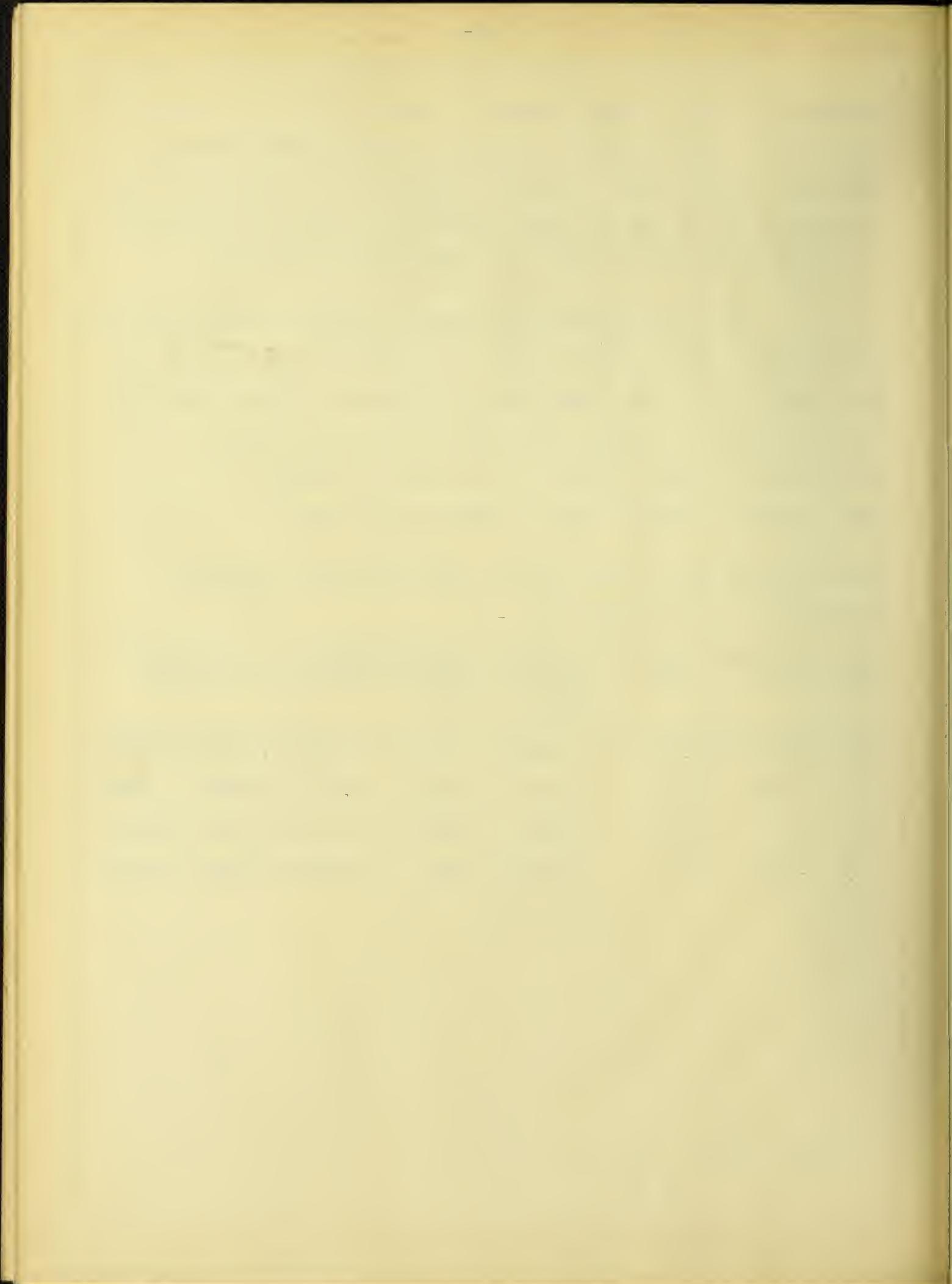
The following results were obtained upon manganese crystals:-

Determination of hydroxylamine --

| No. of Expt. | Wt. Crys. in g. | c.c. Ti Sol. used | Strength of Ti Sol. | Wt. NH_2OH found per c.c. in g. | % NH_2OH found in theory | Formula of Compound |
|--------------|-----------------|-------------------|---------------------|-----------------------------------|----------------------------|---------------------|
|--------------|-----------------|-------------------|---------------------|-----------------------------------|----------------------------|---------------------|

| | | | | | | |
|---|-------|-------|----------|--------|---------------|--------------------------|
| 1 | .0631 | 73.41 | .0001828 | .02768 | 44.09% 43.9% | $MnCl_2 \cdot BNH_2OH$ |
| 2 | .0755 | 57.00 | .00028 | .03294 | 44.09% 43.68% | $Mn_2Cl_2 \cdot 3NH_2OH$ |
| 3 | .1116 | 41.12 | .000271 | .02298 | 20.77% 20.59% | $MnCl_2 \cdot NH_2OH$ |
| 4 | .0931 | 113.8 | .000175 | .0411 | 44.09% 44.14% | $MnCl_2 \cdot 3NH_2OH$ |

+ Blair p.112



Determination of manganese

| No. of Expt. | Wt. Crys. taken in grams | g. $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ | Wt. of MnCl_2 used | % of MnCl_2 theory | % of MnCl_2 found | Formula |
|--------------|--------------------------|--|-----------------------------|-----------------------------|----------------------------|---|
| 1 | 1.1361 | 5.4891 | .6351 | 55.9 | 55.902 | $\text{MnCl}_2 \cdot \text{MNH}_2\text{OH}$ |
| 2 | .1792 | .1219 | .142 | 79.2 | 79.24 | $\text{MnCl}_2 \cdot \text{NH}_2\text{OH}$ |
| 3 | .3482 | 1.681 | .1943 | 55.9 | 55.81 | $\text{MnCl}_2 \cdot 3\text{NH}_2\text{OH}$ |
| 4 | .6178 | 2.9723 | .3455 | 55.9 | 55.82 | $\text{MnCl}_2 \cdot 3\text{NH}_2\text{OH}$ |





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